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A physico-chemical investigation of some magnetically anomalous inorganic compounds

J. R. Snedden
Wollongong University College

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A PHYSICO-CHEMICAL INVESTIGATION OF SOME MAGNETICALLY ANOMALOUS INORGANIC COMPOUNDS

Thesis submitted in partial fulfilment
of the requirements for the degree of
Master of Science

by

J. R. SNEDDEN, B.Sc., A.S.T.C., A.R.A.C.I.

School of Chemistry,
Wollongong University College

June, 1967

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S U M M A R Y

The work described in this thesis is concerned with the anomalous magnetic behaviour of divalent copper complexes of general formulae L Cu X, L^1_3 Cu_2 X^1_2 and L^{11} Cu where L is imidazole, benzimidazole and substituted benzimidazoles; L^1 is benzotriazole; L^{11} is quadridentate derivatives of benzimidazole and α- acyloin oximes; X is chloride and X^1 is chloride or hydroxyl.

The temperature variation of the magnetic susceptibility has been measured over the range 90°K to 450°K. Of the twenty-six complexes investigated, eighteen are described for the first time.

All the complexes are magnetically anomalous. The room temperature magnetic moments are abnormally low and the temperature variation of the paramagnetic susceptibility is complex deviating markedly from simple Curie or Curie-Weiss Law behaviour.

The magnetic behaviour has been rationalised by assuming it to be the sum of two components:

(1) A curie Law component and

(2) A linear antiferromagnetic component.

SUMMARY (Continued)

It is suggested that the Curie Law part of the susceptibility originates mainly from non-interacting end groups and the linear antiferromagnetic component from exchange interactions along chains of bridged copper atoms.

Theoretical curves have been satisfactorily fitted to the experimental data by calculating susceptibility values from an expression derived in terms of the Ising spin model for an infinite chain of interacting copper atoms to which a proportion of Curie Law magnetic susceptibility had been added.

Polymeric structures which may permit linear antiferromagnetism have been postulated for all investigated types of complexes.

****

2.0 THEORY:

The discussion of the work described in this thesis requires a preliminary knowledge of some of the basic terms and ideas of magnetochemistry. A discussion of these forms part of the theoretical introduction.

2.1 MAGNETOCHEMISTRY:

From the basic equation derived by Van Vleck[1], Figgis and Martin[2] have obtained a general equation for magnetic susceptibility. The equation has the form:

$$\chi_m = \frac{N \sum_{nm} \left\{E^{(1)}_{nm}\right\}^2 \Big/ kT - \left\{2E^{(2)}_{nm}\right\} \exp\left\{-E_n^{(0)}\right\} \Big/ kT}{\sum_n g_n \exp\left\{-E^{(0)}\right\} \Big/ kT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where N = Avagadro's Number

k = Boltzmann Constant

T = Absolute Temperature

χ_m = Molar Susceptibility

and $E_{nm} = E_n^{(0)} + E_{nm}^{(1)} H + E_{nm}^{(2)} H^2$ $\ldots\ldots\ldots\ldots\ldots\ldots (2)$

E_{nm} is the total energy consisting of the energy associated with the spin states in the absence of a magnetic field $\left\{E_n^{(0)}\right\}$, the energy associated with the first order Zeeman effect $E_{nm}^{(1)}$, and the energy associated with the second order Zeeman effect $E_{nm}^{(2)}$. The spin degeneracy,

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g_n , of level n and the sublevels removed by the application of a magnetic field are specified by the magnetic quantum number, m. In later discussion, the second order Zeeman term will be shown to be small compared to the first order term and, to a first approximation, may be neglected. Neglecting the second order Zeeman effect, equation (1) reduces to -

$$\chi_m = \frac{N \sum_{nm} \left\{E_{nm}^{(1)}\right\}^2 \Big/ kT \exp \left\{-E_n^{(0)}\right\} \Big/ kT}{\sum_n g_n \exp \left\{E_n^{(0)}\right\} \Big/ kT} \quad \ldots\ldots\ldots\ldots (3)$$

$E_n^{(0)}$ may be defined in terms of the spin, S, associated with the level, m, according to the equation:

$$E_n^{(0)} = JS\,(S + 1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where S is the maximum value of the total spin associated with this level. The energy term, $E_{nm}^{(1)}$ associated with the first order Zeeman effect can assume values in units of $g\beta$ from + $mg\beta$ to - $mg\beta$ where $g\beta$ H is the energy separation between the sublevels in a magnetic field.

The simplest case for the application of equation (3) is an isolated atom with one unpaired electron, i.e. $S = \frac{1}{2}$

For this system, $E_n^{(0)} = -\frac{3}{4} J$

$$E_{nm}^{(1)} = \begin{matrix} + \\ - \end{matrix} \frac{1}{2} S$$

Equation (3) takes the form

$$\chi_m = \frac{\left\{Nk\, g^2\beta^2/kT\right\} \exp\left\{3J/4/kT\right\}}{2 \exp\left(3J/4/kT\right)}$$

$$= \frac{N\, g^2\beta^2}{4\, k} \quad \frac{1}{T} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$= \frac{C}{T}$$

This is known as the Curie Law.

The Curie Law

The Curie Law is of limited validity as it applies only under ideal conditions since it is subject to the same limitations as Langevin's expression.[3] These limitations are caused by Langevin's assumptions that temperature variations do not alter the distribution of the populations among the various magnetic terms; that the temperature independent contribution ($n\alpha$) to the susceptibility must be negligible since α results from terms which are energetically high above the ground term; that the moment must be independent of temperature; and that the interionic interactions must also be absent and hence the substance must be magnetically dilute.

The Curie-Weiss Law

If a plot of the reciprocal of the susceptibility versus temperature is linear but cuts the temperature

axis at some distance Θ, from the origin, the magnetic behaviour may, if Θ is not too large, be described by the Curie-Weiss expression.

$$\chi = \frac{C}{T - \Theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where Θ is the Weiss constant.

Gorter[90] has shown that when there is a thermal equilibrium between two states with different magnetic moments, at sufficiently high temperatures, a linear plot of χ^{-1} against T is obtained. Extrapolation to $\chi^{-1} = 0$, gives a negative Weiss constant when the state preferentially populated at low temperatures is magnetically weaker than the excited state. If the situation is reversed, a positive Weiss constant results.

Diamagnetism

Langevin[3] explained the occurrence of diamagnetism by considering the tendency of all electrons in closed shells to orient their planes of rotation in such a way as to suffer a minimum of interactions with an external imposed magnetic field. The motion of the electrons if treated as charged particles in a magnetic field, may be shown to give their atoms the properties of a magnetic dipole. The magnitude of this dipole is proportional to the magnitude of the applied external field. The electron motion may be represented by a wire loop carrying

an electric current which obeys Lenz's Law. This sign of the dipole is such that the induced magnetic field, ΔH opposes the applied field.

The susceptibility is therefore negative. Diamagnetism which is characteristic of all substances is a very weak effect and is quite often masked by other magnetic effects.

Paramagnetism

The atoms or ions, in which paramagnetism is found, behave as though they have a permanent magnetic moment. When molecules are free to rotate themselves, they are subject to two opposing effects -

(1) the effect of the magnetic field H, which tends to align the atoms or ions in the same direction as that of the imposed magnetic field.

(11) this alignment is counteracted by thermal agitation (kT effect) which tends to randomise it. As a result, the susceptibility decreases with increased temperature.

Paramagnetism arises from the angular momentum and gives the atom the properties of a permanent magnetic dipole. The angular momentum can be either orbital - resulting from the movement of the electron about the nucleus, or spin - when it originates from the effective rotation of the electron about its own axis. The component of the magnetic dipole of the atom in a particular direction

(e.g. z direction) is

$$\mu_z = L_z + S_z \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where L_z and S_z are the sums of the components of the orbital and spin angular momenta for the electrons in the atom in the z direction. Table 1 lists the calculated and observed magnetic moments for elements of the first transition series.

2.2 ORBITAL CONTRIBUTION

For ions or atoms which exhibit orbital contribution to the magnetic moment, the magnetic moment can be expressed as:

$$\mu^2 = L(L + 1) + 4S(S + 1)$$

This expression relates the magnetic moment with the spin angular momentum S, and the orbital angular momentum L.

It has been shown for members of the first transition series elements that the magnetic moment is better expressed by -

$$\mu^2 = 4S(S + 1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

In this expression, the orbital contribution has been neglected because the orbital angular momentum is quenched by ligand fields for the elements of the first transition series for which this expression holds.

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TABLE 1

CALCULATED AND OBSERVED MAGNETIC MOMENTS FOR ELEMENTS OF THE FIRST TRANSITION SERIES[4]

Total No. of d Electrons	No. of $d\gamma$ Electrons	No. of $d\varepsilon$ Electrons	Ground State Quantum Nos. S	L	μ_S	μ_{S+L}	Observed Moments (B.M.)	Ions
1	0	1	$\frac{1}{2}$	2	1.73	3.0	1.7-1.8 1.7	V(1V) Ti(111)
2	0	2	1	3	2.83	4.47	2.8-2.9 3.8-3.9	V(111) V(11)
3	0	3	$\frac{3}{2}$	3	3.88	5.20	3.8-4.0 3.7-3.9	Mn(1V) Cr(111)
4	0	4	1	3	2.83	4.47	3.2-3.3 3.2	Cr(11) Mn(111)
4	1	3	2	2	4.90	5.48	4.8-4.9 4.9-5.0	Cr(11) Mn(111)
5	0	5	$\frac{1}{2}$	2	1.73	3.0	2.0-2.5	Fe(111)
	2	3	$\frac{5}{2}$	0	5.92	5.92	5.7-6.1 5.9-6.0	Mn(111) Fe(111)
6	0	6					--	
	2	4	2	2	4.90	5.48	5.1-5.7	Fe(11)
7	1	6	$\frac{1}{2}$	2	1.73	3.0	1.7-2.0	Ni(111)
	2	5	$\frac{3}{2}$	3	3.88	5.20	4.3-5.2	Co(11)
8	2	6	1	3	2.83	4.47	2.8-3.5	Ni(11)
9	3	6	$\frac{1}{2}$	2	1.73	3.0	1.7-2.2	Cu(11)

By definition it may be said that an electron will contribute to the orbital angular momentum if it is possible to convert the orbit in which the electron is located into an equivalent and degenerate orbital by rotation about an axis.

The rotation of a free ion about the z axis through 45° converts the $d_{x^2 - y^2}$ orbital into the d_{xy} orbital. This equivalence gives to the ion an orbital angular momentum of $\pm 2 \frac{h}{2\pi}$ units, depending upon the sense of rotation. Similarly, rotation of the d_{xy} into the d_{yz} orbital through 90° contributes $\pm$ 1 unit of orbital angular momentum. The d_{z^2} orbital obviously does not contribute to the orbital angular momentum about this axis. Schematic representation of $d\gamma$ and $d\varepsilon$ orbitals is shown in figure 1.

This degeneracy may be destroyed by a ligand field in a complex compound. In an octahedral complex the $d\varepsilon$ orbitals are separated from the $d\gamma$ orbitals by an energy difference as shown in figure 2. The $d_{x^2 - y^2}$ orbital is no longer equivalent to the d_{xy} orbital and rotation is no longer possible since the energy barrier is too great. Consequently, the contribution of 2 units of orbital angular momentum no longer occurs. The d_{xy} and d_{yz} orbitals are, however, still degenerate and may contribute 1 unit of orbital angular momentum and consequently the orbital contribution to the magnetic moment or ion.

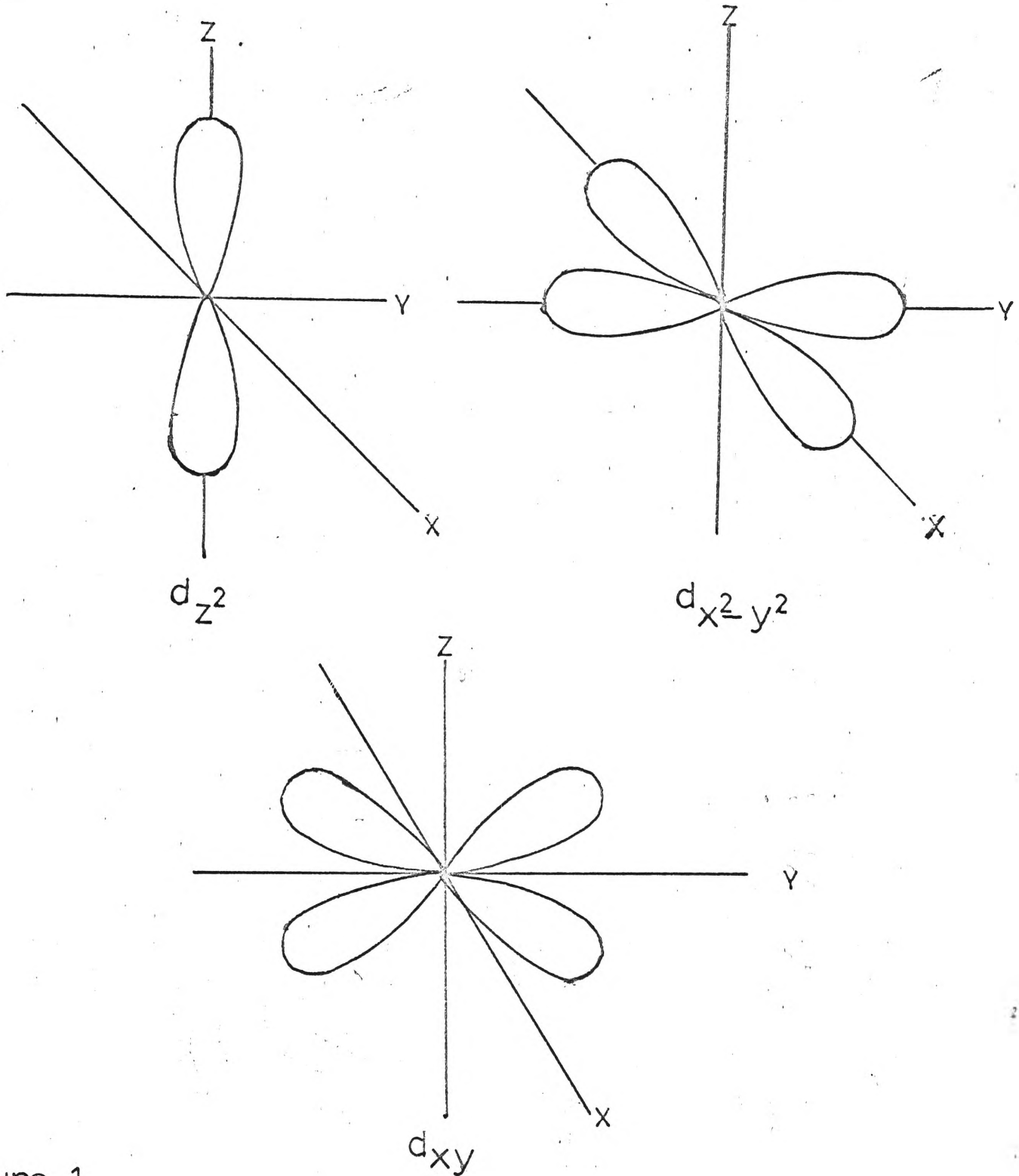
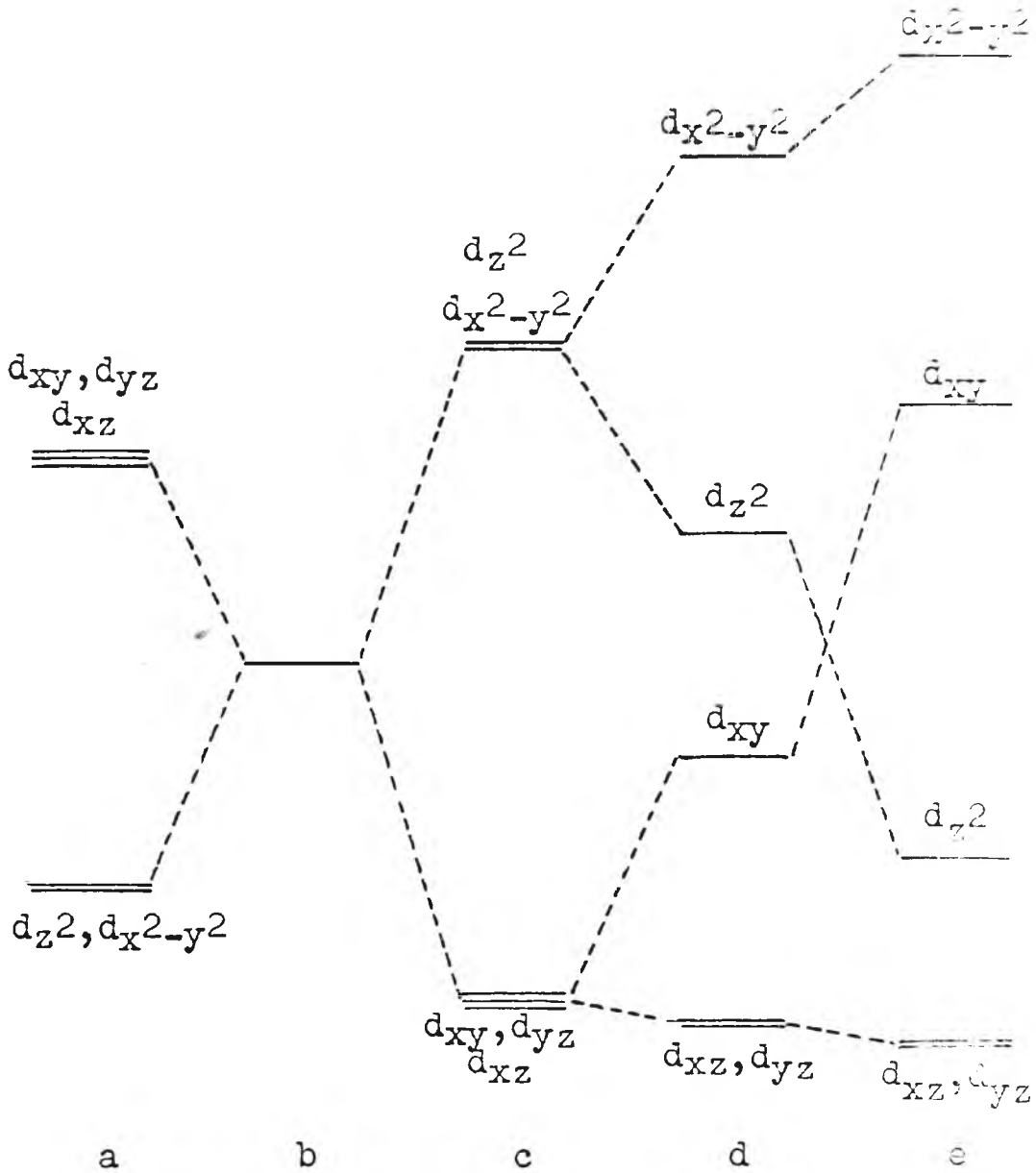


Figure 1

Schematic representation of d_γ and d_ε orbitals.

Fig.2. MODIFICATION OF d-ORBITAL.



Modification of d-orbital energy levels as a result of changes in the geometry of the ligand field.

Code. a - Tetrahedral
b - Free Ion
c - Octahedral
d - Tetragonal or square pyramid
e - Square planar

Spin-Orbit Coupling

The energy levels of electrons in an atom or ion are specified by the four quantum numbers - N, L, M_L and M_S. The combined action of the mutual repulsion between the electrons in the shell is the most important effect in lifting the degeneracy of a set of energy levels. The result of these perturbations is the splitting of the degenerate energy levels into terms. The energy level terms are separated by energies of the order of 10^4 cm^{-1}.

The energy levels are usually degenerate and may be split by LS coupling, where S is the total spin and L is the total orbital angular momentum of the atom. The total degeneracy of a term is the product of the degeneracies in the orbital and spin angular momentum which is equivalent to $(2S + 1)(2L + 1)$. Spin-orbit coupling arises from the interaction of the magnetic moments associated with L and S. The ground state which is of greatest interest in magnetochemistry may be deduced by using Hund's rules. The ground states are shown in Table 2 for the first transition series.

It is found on examination of Table 2 that the electrons have been arranged so as to give the largest possible value of M_L and hence the largest value of L consistent with as many electrons as possible being unpaired.

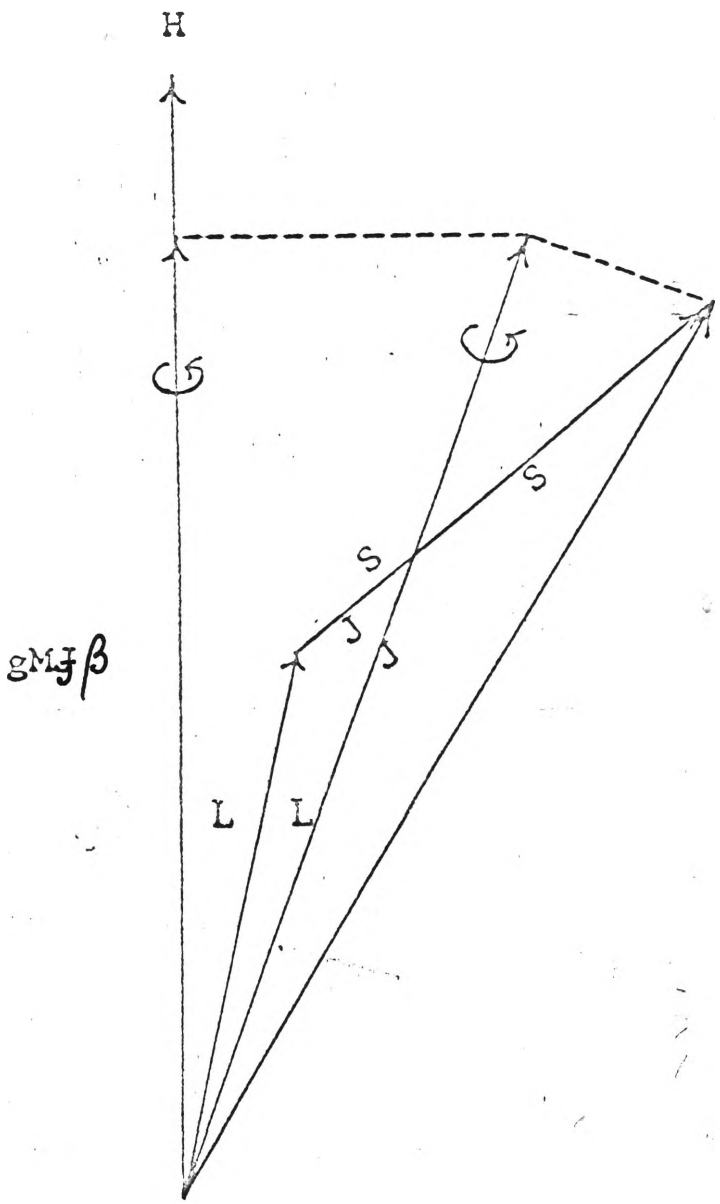
TABLE 2

GROUND STATES FOR THE FIRST TRANSITION SERIES

No. of *d* Electrons	Ground Term and State	M_L	M_S	J
1	$^2D_{\frac{3}{2}}$	2	$\frac{1}{2}$	$\frac{3}{2}$
2	$^3F_2$	3	1	2
3	$^4F_{\frac{3}{2}}$	3	$\frac{3}{2}$	$\frac{3}{2}$
4	^5D_o	2	2	0
5	$^6S_{\frac{5}{2}}$	0	$\frac{5}{2}$	$\frac{5}{2}$
6	$^5D_4$	2	2	4
7	$^4F_{\frac{9}{2}}$	3	$\frac{3}{2}$	$\frac{9}{2}$
8	$^3F_4$	3	1	4
9	$^2D_{\frac{5}{2}}$	2	$\frac{1}{2}$	$\frac{5}{2}$

If spin-orbit coupling occurs, energy levels are further split into states or multiplets, and each state is specified by the total angular momentum quantum number J. The interaction leads to a precession of L and S about a common axis, the greater the interaction between L and S the faster will be the precession of L and S and therefore, the greater

Fig. 3 ADDITION OF MAGNETIC MOMENTS IN AN ATOM



The length of μ_L equals the length of L, μ_S is therefore twice the length of S.

the difference in energies of the states with different total angular momentum. This results in larger multiplet splitting.

For each value of J, there are (2J + 1) possible orientations of J in an external magnetic field and hence there are (2J + 1) possible values of J (see figure 2).

The vectorial addition of S and L is shown diagramatically in figure 3. The magnetic vector, μ_s has been drawn twice the length of S, because 1 unit of S gives twice the magnetic moment of 1 unit of L. The addition of μ_s and μ_L gives the resultant μ, which does not coincide with the direction of J but precesses about it. In calculations of the magnetic moment, μ_J, the component of μ in the direction of J is considered. In the external magnetic field the component of the magnetic moment in the direction of the field is $gM_J\beta$

In the absence of a magnetic field, each state designated by a particular J value is (2J + 1) fold degenerate and from each energy level arises (2J + 1) or (2S + 1) states (whichever is the lesser).

Recent reviews[5, 6] on magnetism have considered the spectroscopic states set up as a result of spin-orbit coupling. The magnetic moment of an ion has been calculated by the equation:

$$\mu = \mu_o \left\{ 1 - \frac{\alpha\lambda}{10D_q} \right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where μ_o is the spin only value of the moment and $10D_q$ is the ligand field splitting. The values of α and λ are characteristic of the degree of spin-orbit coupling taking place. The spin-orbit coupling constant, when written as λ, applies to the ground term for the whole set of d electrons and must be used in conjunction with $\alpha\lambda$. If the ion under consideration is spin paired, then λ ceases to have its normal significance and has to be replaced in equation (8) by ζ, the spin coupling constant per electron $\alpha\lambda$ is replaced by $\alpha\zeta$. Table 3 lists the values of the four constants for some of the elements of the first transition series.

It may be seen from Table 3 that the values of λ and ζ are very much greater for configurations above d^5 than they are for configurations below d^5 and that for the manganous and ferric ions, no spin coupling is anticipated and so μ may be expected to be equal to μ_o. Table 3 shows that the spin-orbit coupling is negative when the d- subshell is more than half full.

McClure[7] has reported values of Dq for several first transition series aquated metal ions (Table 4).

TABLE 3

SPIN-ORBIT COUPLING CONSTANTS FOR ELEMENTS OF THE FIRST TRANSITION SERIES

Ion	$\alpha\lambda$	λ	$\alpha\zeta$	ζ
Ti(111)	2	154	2	154
V(111)	4	108	2	217
Cr(111)	4	91	$\frac{4}{3}$	275
Cr(11)	2	57	$\frac{1}{2}$	229
Mn(111)	2	88	$\frac{1}{2}$	352
Fe(111)	0	-	0	395
Mn(11)	0	-	0	440
Fe(11)	2	-102	$-\frac{1}{2}$	408
Co(11)	4	-177	$-\frac{4}{3}$	530
Ni(11)	4	-315	-2	630
Cu(11)	2	-829	-2	829

TABLE 4

Dq DATA FOR THE HEXAHYDRATED IONS OF THE FIRST ROW TRANSITION METALS[7]

No. of d Electrons	Metal	Dq (cm^{-1})
1	Ti(111)	2030
2	V(111)	1800
3	V(11)	1180
	Cr(111)	1760
4	Cr(11)	1400
	Mn(111)	2100
5	Mn(11)	750
	Fe(111)	1400
6	Fe(11)	1000
7	Co(11)	1000
8	Ni(11)	860
9	Cu(11)	1300

Let us consider the application of equation (8) to the $\{Cu\ (H_2O)_6\}^{2+}$ ion. On substituting the value 13000 cm^{-1} for 10Dq, ℓ for $\propto\lambda$ and -829 for λ in equation 8, a value of 1.96 B.M. is obtained for the magnetic moment. This value compares favorably with the reported value of 1.93 B.M. for Tutton's salt, $K_2Cu(SO_4)_2 \cdot 6H_2O$ in which copper is known to be present as the $\{Cu\ (H_2O)_6\}^{2+}$ ion. The usefulness of McClure's Dq values is often limited by their unreliability.

The First Order Zeeman Effect

For a configuration in which the Russell-Saunders coupling holds, the application of a magnetic field removes the remaining degeneracy of each state of the free ion. The change in energy is proportional to H. Each state is split into (2J + 1) components lying at energy $M_J g\beta H$ where β is the Bohr Magneton and g is the Landé or spectroscopic splitting factor.

The Landé splitting factor g is equivalent to:

$$g = \frac{1 + J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \quad \ldots\ldots\ldots\ldots (9)$$

g is a proportionality factor by which one must multiply J in order to obtain the magnetic moment due to J. It arises from the fact that the magnetic moment associated with the spin angular momentum is twice as large as that associated with the orbital momentum. Therefore, when

the moment is derived from the spin only, then $g = 2$; when from L only then $g = 1$, and when the moment is derived from both L and S, g is usually between one and two.

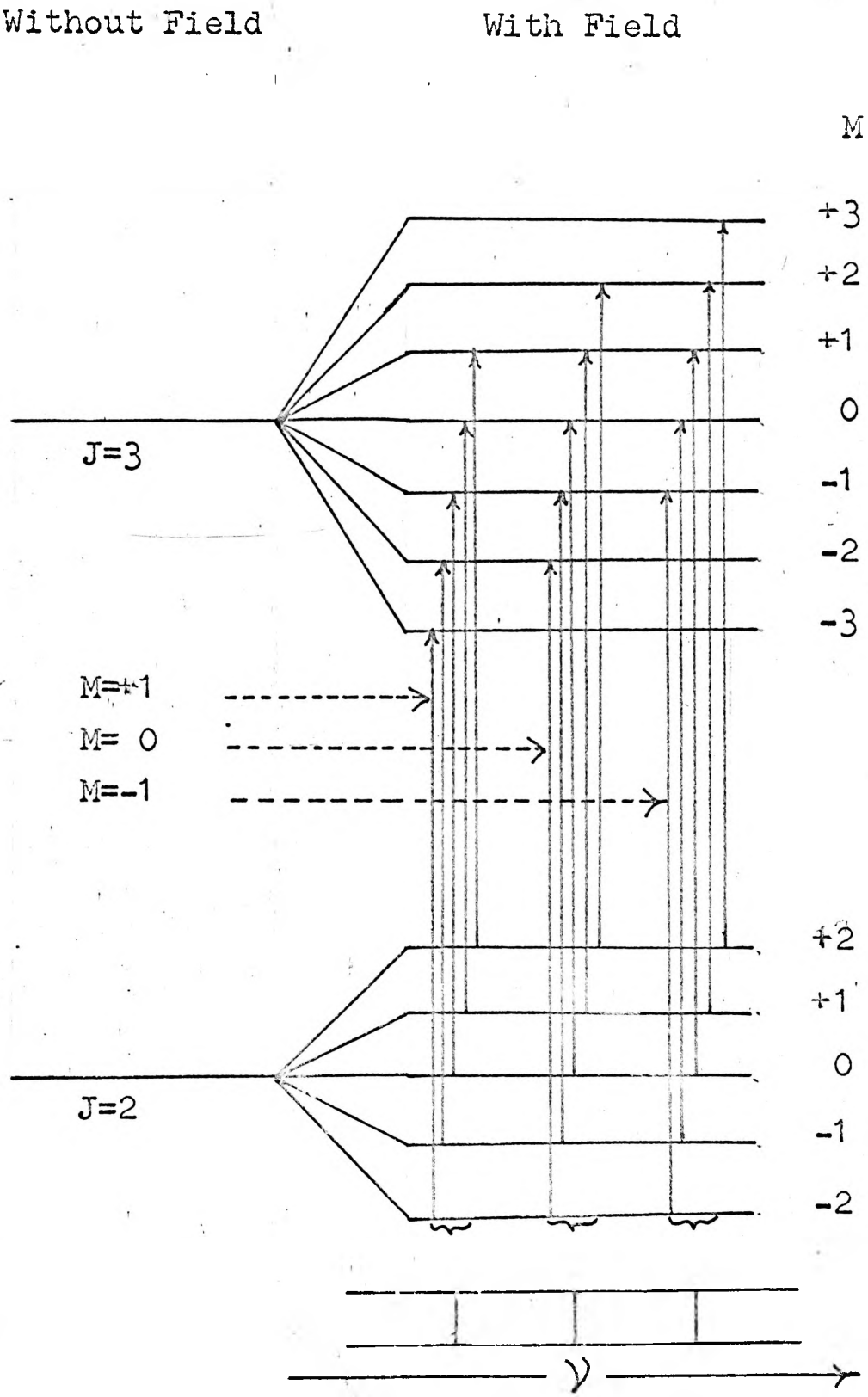
The splitting of $J = \frac{3}{2}$ and $J = 2$ is shown in Figure 4. For a magnetic field of approximately 10^4 gauss, the splitting of the states by the applied field is of the order of a few reciprocal centimetres which is small compared to the thermal energy, kT.

The Second Order Zeeman Effect

In equation 2, only the first two terms have been considered and it is the third term in H^2 which describes the second order Zeeman effect. The external magnetic field distorts or polarises the electron distribution in the unfilled shell of the atom or ion. This polarisation is equivalent to 'mixing in' of higher states with the ground state and vice versa.

The whole set of levels of the ground state is lowered energetically and the levels of the higher states with which the 'mixing' takes place are raised. Thus there is an overall shift in the centre of gravity of the involved states with the second order Zeeman effect. If the higher is much higher than the ground state ($E \rightarrow kT$), there is a contribution to the susceptibility, which is independent of temperature. This temperature independent contribution to the susceptibility decreases in value with increasing

Fig 4a. THE NORMAL ZEEMAN EFFECT



The normal Zeeman effect for a combination J=3 J=2. The arrows in each group are of equal length, and give therefore, rise to the same line in the splitting pattern.

energy of the 'mixed in' high level.

If the level which is 'mixed in' lies much higher than kT above the ground state, thermal distribution between the levels does not occur, and the contribution to the susceptibility is therefore, temperature independent. If the levels above the ground state are seperated from it by an energy which is large, but not infinitely large compared to kT, the susceptibility is given by:

$$\chi_A = \frac{C}{T} + N\alpha \quad \text{.....(10)}$$

where $N\alpha$ is the temperature independent paramagnetism and N is Avagadro's number.

For Cu^{2+}, the temperature independent paramagnetism adds about 60×10^{-6} c.g.s. units to the χ_M of about 1500×10^{-6} c.g.s. units at room temperature.

Ferromagnetism and Antiferromagnetism

Whereas paramagnetism is a property of an individual ion or atom, both ferromagnetism and antiferromagnetism are associative phenomena. Both are functions of exchange interactions between electrons of paramagnetic ions in, chiefly, magnetically concentrated substances.

Consider two metal atoms in close proximity with angular moments of S_i and S_j respectively. The interaction between these two atoms may be described as the setting up of two energy levels in one of which S_i and S_j are in the same

direction and in the other, in opposite directions. This spin-spin coupling may be formally represented as $E = J S_i S_j$, where J is known as the exchange coupling constant or simply as the exchange integral. By convention, -J indicates that the level with antialigned spins lies lowest whilst +J indicates that the level with aligned spins lies lowest. The condition that J is positive gives rise to ferromagnetism whilst antiferromagnetism is obtained when J is negative.

Ferromagnetism

In ferromagnetic substances spins are aligned parallel to each other over small regions in crystal lattices, called domains. The exchange forces which hold the spins parallel against thermal agitation are positive, field strength dependent and of a magnitude of several million oersteds but they are effective only over distances of the order of molecular dimensions. Above the Curie temperature these materials become paramagnetics; the susceptibilities of ferromagnets are dependent upon field strength below the Curie Point.

Antiferromagnetism

A J value associated with antiferromagnetism is negative. Antiferromagnetism may be defined as paramagnetism extending over more than one magnetic centre, characterised by a negative exchange coupling constant which is reflected in a lowering of the effective spin.

For a typical antiferromagnetic compound, the susceptibility rises sharply as the temperature rises, to reach a maximum, above which the thermal agitation is stronger than the exchange forces. The Curie or Curie-Weiss law is again obeyed. The temperature at which the susceptibility reaches a maximum is known as the Curie temperature. The magnetic exchange in such a system results from a dipolar coupling between the angular momenta on the interacting ions.

This coupling has been shown to concern the spin angular momenta; formally written as $S_i S_j$. It is possible to derive theoretical expressions which describe the magnetic behaviour of such compounds exactly. For example, copper acetate dihydrate has an effective magnetic moment which is equivalent to:

$$\mu_{eff} = \mu^{o}_{eff} \left\{ 1 + \frac{1}{3} e^{\frac{2J}{kT}} \right\}^{-\frac{1}{2}} \qquad \text{.....(11)}$$

where μ^{o}_{eff} is the magnetic moment in the absence of exchange.

Intramolecular Antiferromagnetism

Intramolecular antiferromagnetism is observed in compounds in which the exchange interaction is confined to paramagnetic centres within one molecule. The compound, $K_4 Ru_2O Cl_{10}$ is an example since it has been shown to contain a linear Ru-O-Ru linkage. Each Ru^{4+} ion would be expected to possess two unpaired electrons each. As the result of antiferromagnetic exchange demagnetisation

between the two Ru^{4+} ions, the complex is diamagnetic.

Intermolecular Antiferromagnetism

If intermolecular antiferromagnetism occurs, magnetic exchange takes place over the whole crystal. At temperatures below 20°K, a small degree of exchange may have a large effect on the magnetic behaviour and therefore antiferromagnetic behaviour may be present in compounds which are magnetically normal at room temperature.

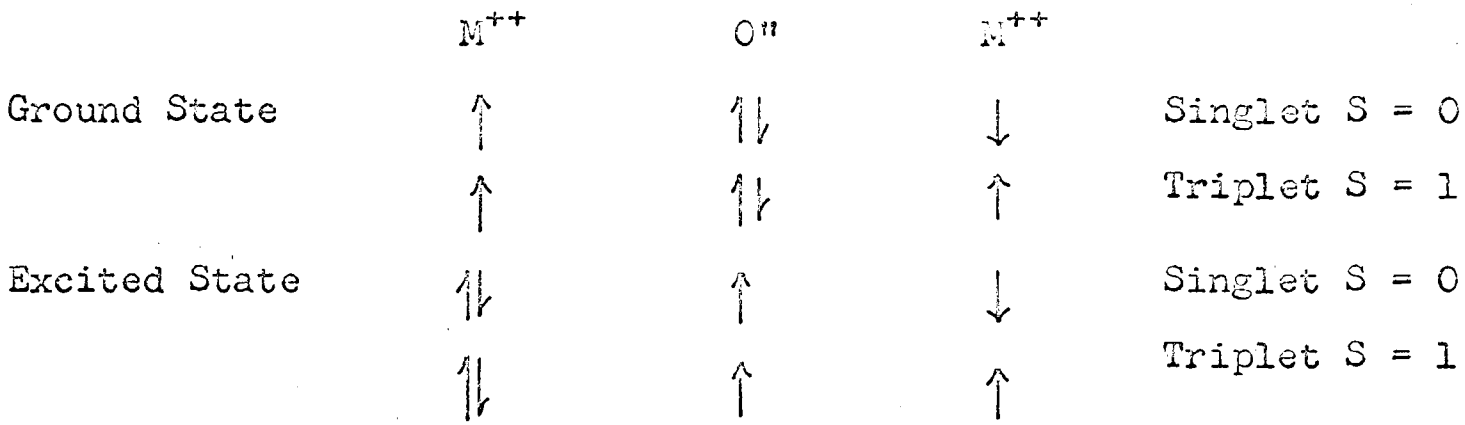
In highly symmetric compounds, the observed antiferromagnetism results from the fact that the alignment takes the form of interpenetrating ferromagnetic lattices of opposite spins, two or more in number. At temperatures well above the Curie temperature, a normal antiferromagnetic substance follows the Curie-Weiss law with a value of Θ which may be related to the exchange integral J, and the Curie temperature, Tc, in a manner which depends on the structure of the compound.

Superexchange and Kramer's Superexchange Theory.[8]

The antiferromagnetic behaviour of oxides such as MnO, FeO, CoO and NiO, has been shown by neutron diffraction studies to be due to the tendency of half the ions to have their magnetic moments lined up in the opposite direction to those of the other half of ions. The scheme for Kramer's exchange is shown in figure 5. The metal d-orbital containing the impaired electron overlaps a

-orbital of the oxygen atom and an electron of opposite

FIGURE 5. SCHEME FOR KRAMER'S SUPEREXCHANGE INTERACTION.



spin from the O^{2-} (oxide) ion will move so as to partially occupy the d-orbital. The remaining π -electron moves to some extent into the d-orbital of the next M-atom. This d-electron must oppose the spin of the entering π -oxygen electron and is therefore in an antiparallel state to the d-electron in the first metal atom. The two d-electrons are in effect coupled. If this state is of lower energy, the lattice as a whole will couple up, lowering the temperature. The susceptibility will consequently drop. This mode of exchange interaction which utilizes the intervening diamagnetic atoms, or even groups of atoms, is known as superexchange or Kramer's superexchange.

2.3 COPPER (11) - COPPER (11) INTERACTION

The interaction of two copper (11) atoms, each of spin $\frac{1}{2}$, is the simplest case of metal-metal interaction and hence will be discussed in some detail. The allowed spin states are $S = 2/2$ and $S = 0/2$ and when substituted into equation (3) the energies associated with these spin states are seen to be:

$$E_o^{(o)} = -0J = 0 \text{ and } E_1^{(o)} = -ZJ$$

With respect to the magnetic field, each state has a degeneracy of $(2S + 1)$. Two states are formed, the upper triplet and lower singlet state. Figure 6 shows the energy diagram for two intersecting copper (11) atoms

FIGURE 7 Structure of Copper(II) Acetate Monohydrate

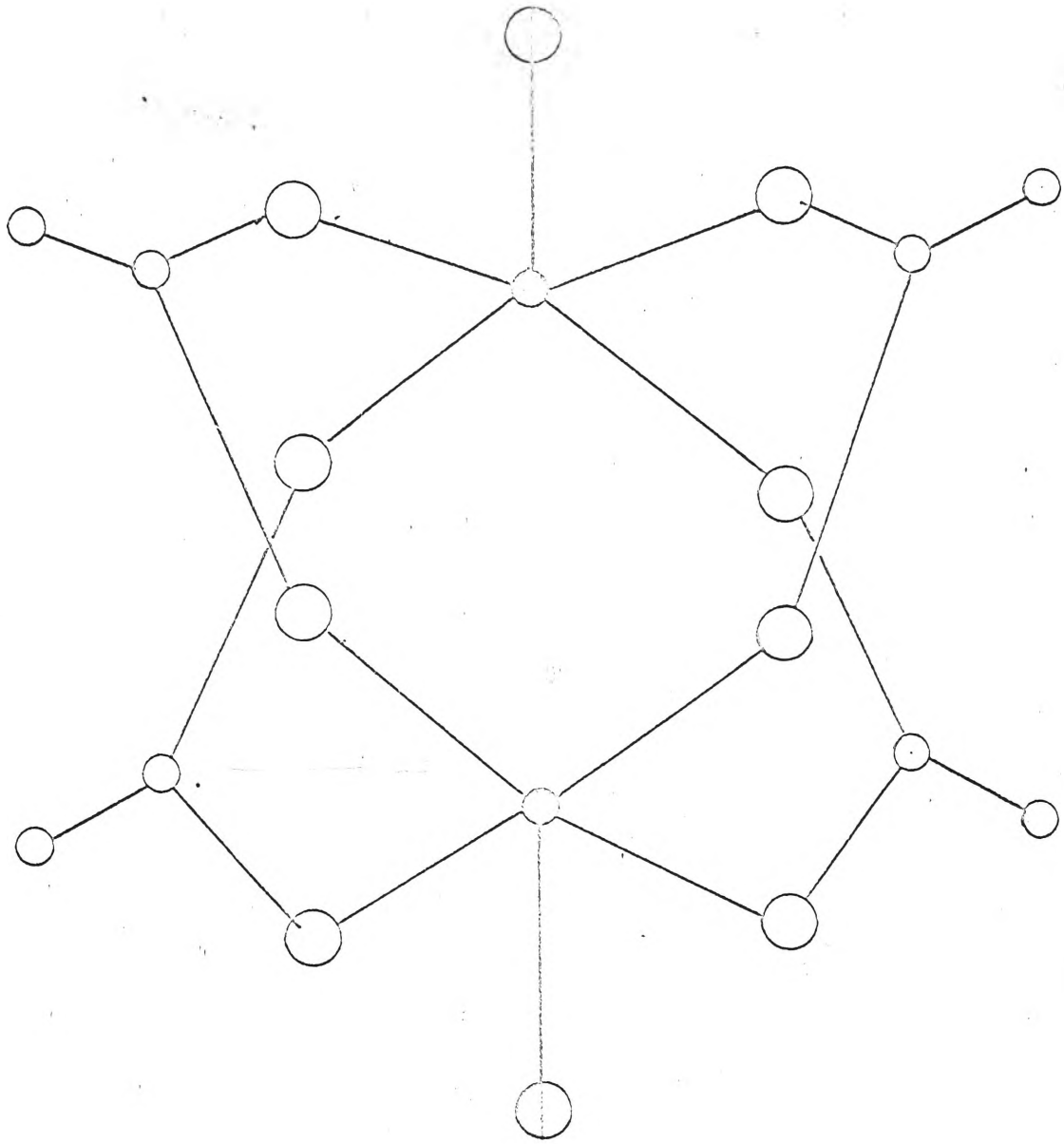
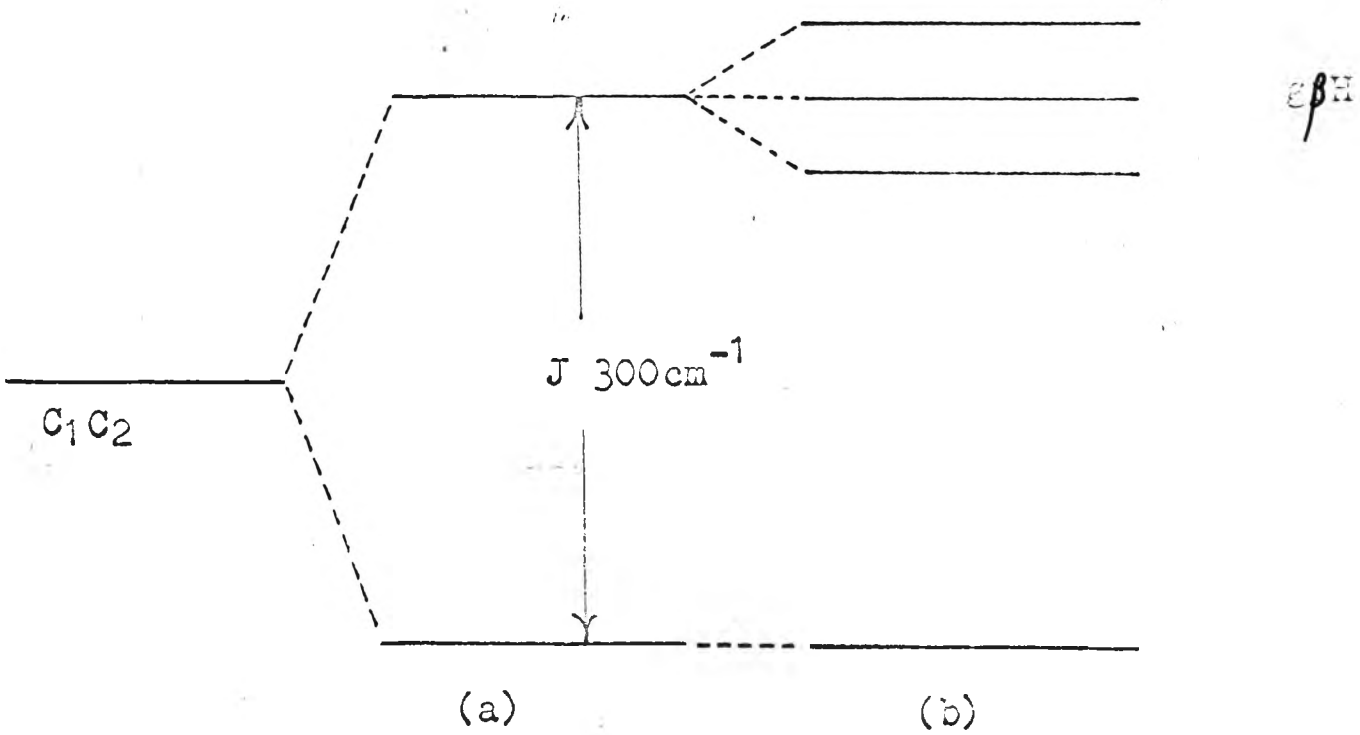


Fig.6 ENERGY LEVEL DIAGRAM FOR THE SPLITTING OF THE LOWEST ENERGY LEVEL OF TWO INTERACTING CUPRIC IONS DUE TO EXCHANGE INTERACTION (a) AND SUPERIMPOSED MAGNETIC FIELD (b).

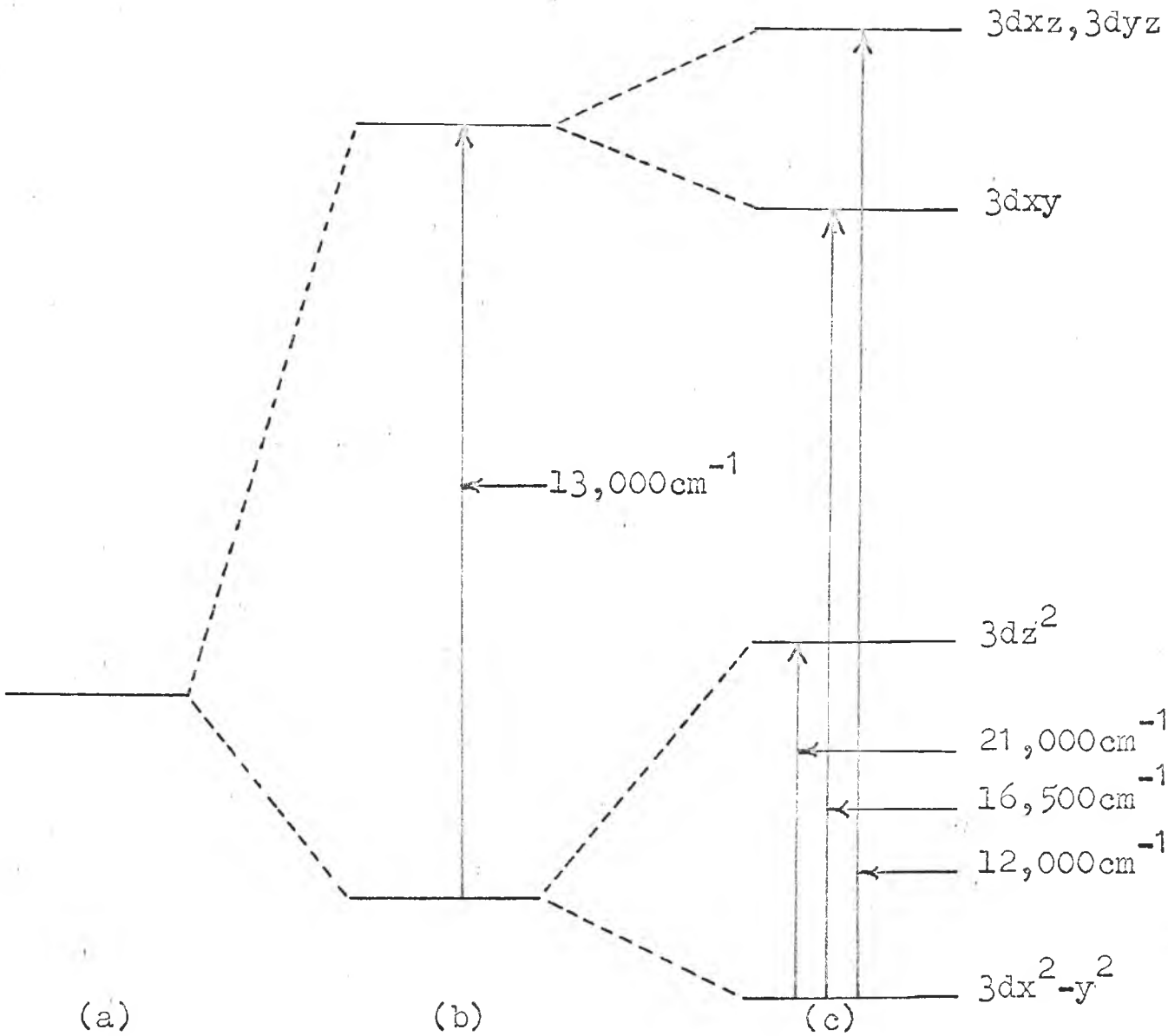


arising from the exchange interaction and from the application of a magnetic field. The energy difference between these two states is equal to -2J. If these values for spin state energies are substituted into equation (11), the Bleany-Bower's equation is obtained.

$$\chi_M = \frac{2g^2\beta^2N}{3kT}\left\{\frac{3\exp(2J/kT}{(1+3\exp(2J/kT)}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Lifschitz and Rosenbohm[10] found that the room temperature susceptibility of copper (11) acetate monohydrate was much lower than normally observed for copper (11) compounds. The variation of magnetic susceptibility with temperature was studied by Guha[11], Foex et al[12]. Figgis and Martin[13] reinvestigated the magnetic susceptibility of copper acetate monohydrate over a temperature range and interpreted the anomalous magnetic behaviour in terms of a delta-bond resulting from lateral overlap of two $3d_{x^2-y^2}$ orbitals on adjacent copper atoms in the binuclear copper acetate molecule with their lobar planes parallel to each other (figure 7). Their argument was based upon the ligand-field splitting calculated by Polder[14] for the $\left\{Cu\ (H_2O)_6\right\}^{2+}$ ion. The splitting pattern in figure 8 is the result of a tetragonal field and of a spin orbit coupling perturbation acting on a free copper (11) ion in a $^2D\ 5/2$ state. In a cubic field, the five fold degenerate level of the free copper (11) ion splits into a lower triply degenerate $d\varepsilon$ level and an upper double degenerate $d\gamma$ level. The

Fig.8 ENERGY LEVEL DIAGRAM FOR d^9 (Cu^{2+}) CONFIGERATION



Energy level diagram for the d^9 configeration of Copper(11) without external field (a); in a cubic symmetry (b); and in a tetragonal field (c).

The tetragonal component lifts the degeneracy of the $d\gamma$ level with the formation of an upper $3d_{x^2-y^2}$ and a lower $3d_{z^2}$ level. The $d\varepsilon$ splits into an upper $3d_{xy}$ and a lower doubly degenerate level, comprising the $3d_{yz}$ orbitals, which split further under the action of spin-orbit coupling, so that all except the spin degeneracy is removed.

On the basis of the ligand field splitting diagram, Figgis and Martin[13] assigned the odd electron to the $4d_{x^2-y^2}$ orbital on each copper atom, thus establishing the feasibility of δ bond formation. Ross[15] re-examined the published paramagnetic resonance spectrum and pointed out that the experimental g values can only be explained by bond formation. Ross and Yates[16] calculated the J values of δ $(3d_{x^2-y^2} - 3d_{x^2-y^2})$ and σ $(3d_{z^2} - 3d_{z^2})$ bonds in copper (11) acetate. They found that the J value is increased to the experimental value of 300 cm^{-1} if orbital expansion occurs under the influence of the ligand field. Ross and Yates[16] also suggested that 'mixing in' a few percent of σ character in the δ bond would result in the observed J value. The interaction between the two copper atoms leads to the formation of a lower lying diamagnetic singlet level and an upper paramagnetic triplet level. The population of the levels is temperature dependent and the susceptibility under these conditions is given by equation (13), the Bleany-Bower's equation. The work on copper (11) acetate monohydrate has been extended

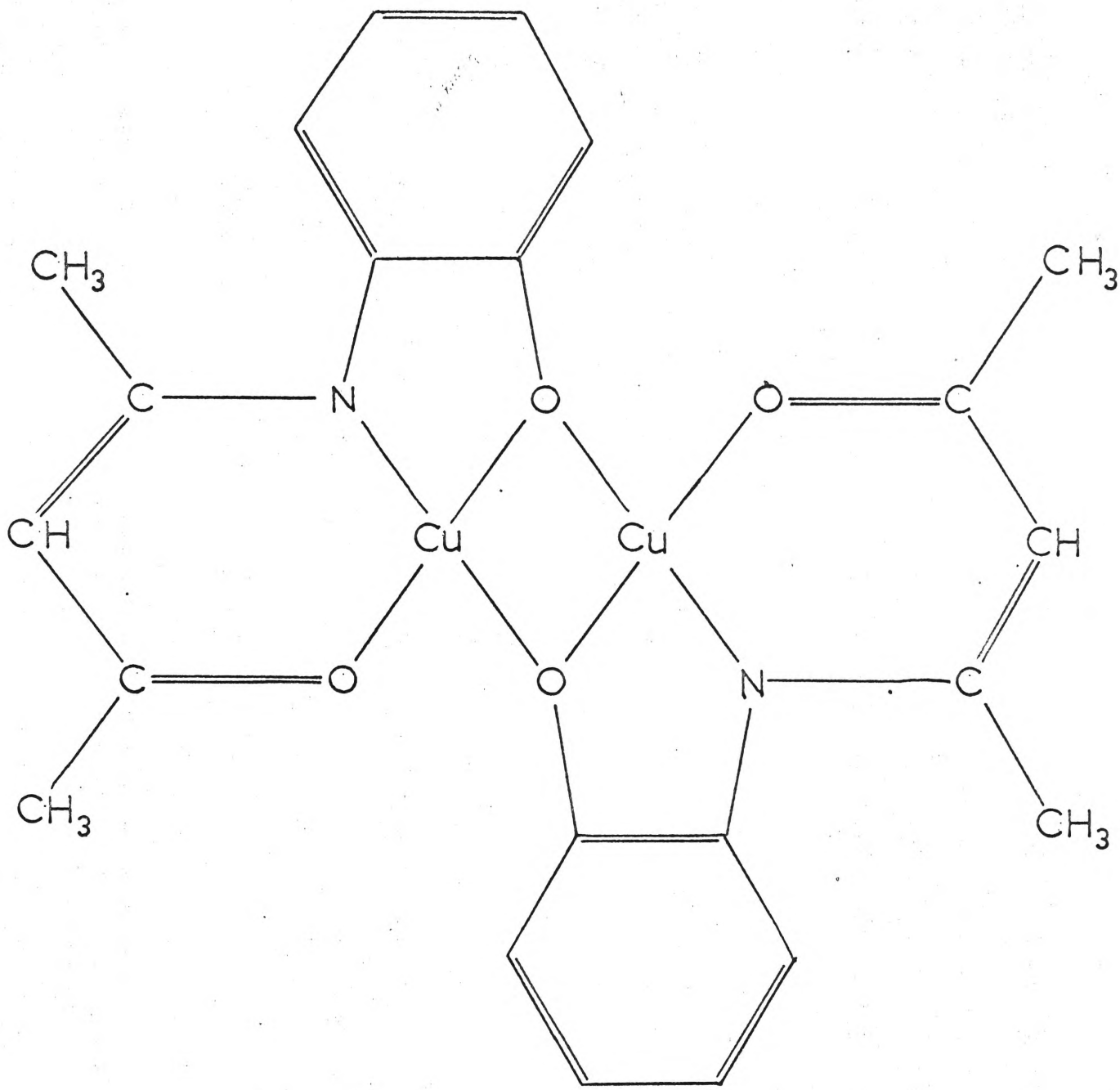


FIGURE 9. STRUCTURE OF ACETYLACETONE -MONO- (O-HYDROXYANIL) COPPER(11).

by these and other workers[17-40, 83] to include a large number of alkanates and mono and dicarboxylic aliphatic as well as aromatic carboxylic acids for many of which the copper acetate type of magnetic behaviour has led to the postulation of binuclear bridged copper acetate type structures.

Kishita, Muto and Kubo[41, 42, 43] prepared a series of copper (11) complexes with tridentate Schiff's bases, all of which contained a nitrogen and two alcoholic or phenolic oxygen donor atoms. Barclay et al[44] investigated the magnetic properties of the compound acetylacetone-mono-(O-hydroxyanil) copper (11). The variation of magnetic susceptibility with temperature was described in terms of the Bleany-Bower's equation. A dimeric structure was postulated by these workers for this compound and was confirmed by a full X-ray analysis. Although the structure of this compound (figure 9) is different to that of copper (11) acetate monohydrate, their magnetic behaviour is very similar.

Co-ordination compounds of pyridine-N-oxide with a variety of transition metal perchlorates and halides have been reported[19, 45, 46] and the infra-red[47, 48] and electronic spectra[46] of some of these compounds have been studied. Carlin[46] isolated the complex Cu $(C_5H_5NO)_n \left(ClO_4\right)_2$ where n = 4 or 6. Quagliano et al[45] prepared Cu $(C_5H_5NO)Cl_2$, Cu $(C_5H_5NO)_4 (ClO_4)_2$ and Cu $(C_5H_5NO)_2 (NO_3)_2$, for which room temperature magnetic moments of 0.85, 0.63 and 1.62 B.M. respectively were obtained.

is above the spin-only value[55]. The magnetic moment of 1.38 B.M. has been obtained for $KCuF_3$[56, 57]. The anomalously low magnetic moment of this compound has been explained in terms of superexchange involving an infinite -M-F-M-[58] bridging arrangement.

Baraclough and Ng[59] have used the equation:

$$M = N \sinh \frac{\mu H}{kT} \left\{ \exp \left(\frac{-4J}{kT}\right) + \sinh^2 \frac{\mu H}{kT} \right\}^{-\frac{1}{2}} \quad \ldots\ldots (13)$$

where M = Magnetic moment per mole at $T^{\circ}K$ in an external magnetic field H

μ = Magnetic moment per atom

to explain the magnetic behaviour of the linear polymers copper (11) chloride and copper (11) bromide. The equation was derived from an equation of Newell and Montroll[60], which was based upon the Ising model. The Ising model allows for interaction between neighbouring atoms and assumes that if a pair of adjacent atoms have their spins parallel, there is an interaction energy of -J. If the electron spins are antiparallel, the interaction energy is assumed to be +J. When J is negative, antiferromagnetism occurs.

For copper (11) ions, with one unpaired electron, $\mu = \frac{g\beta}{2}$

where g = spectroscopic splitting factor

β = Bohr magnetron.

STRUCTURE OF PYRIDINE -N- OXIDE COPPER(11) COMPLEXES.

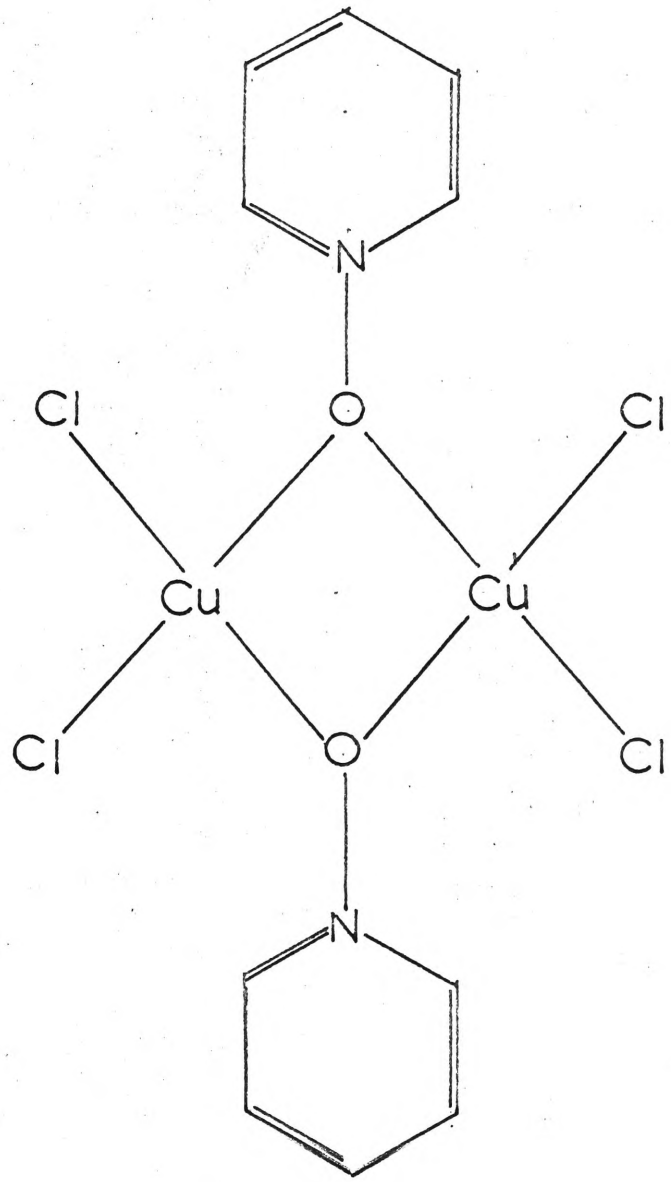


FIGURE 10 a.

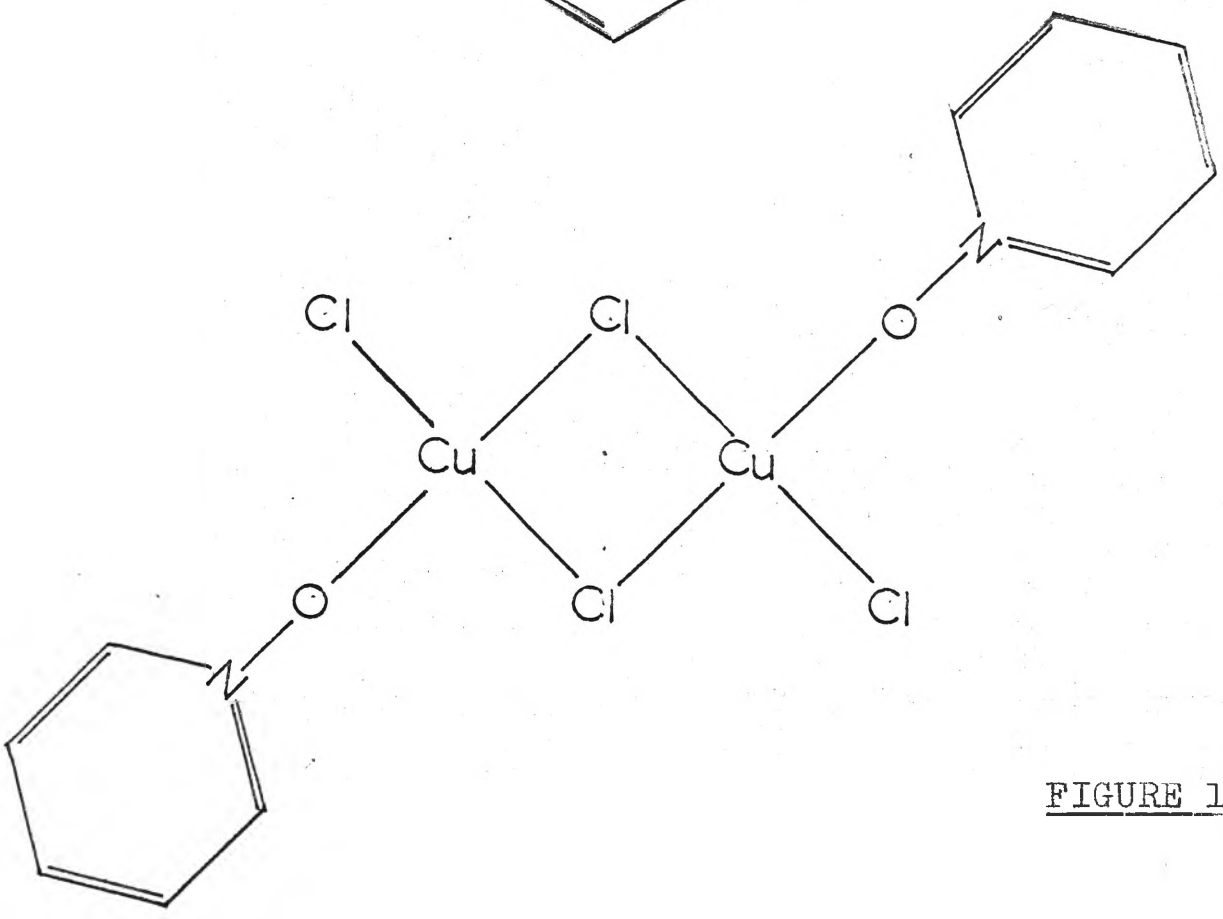


FIGURE 10 b.

Harris et al[19] prepared and independently studied the anomalous paramagnetism of a series of pyridene - and quinoline-N-oxide complexes of copper (11). The anomalous paramagnetism of the pyridine-N-oxide complex, $Cu(C_5H_5NO)Cl_2$, was confirmed and the analogous copper (11) bromide complex was also shown to be magnetically anomalous. They related this anomalous magnetic behaviour to a thermal equilibrium between a lower singlet state and an upper triplet state approximately 2 K. cal. apart. Structure (a) was postulated rather than the halogen bridged structure (b) shown in figure 10, since a binuclear oxygen bridged arrangement had been predicted from magnetic studies for the copper (11) complex of acetylacetone-mono-(-O-hydroxyanil) and this structure was subsequently confirmed by X-ray structural analysis[49]. Other workers[42, 50, 51] support this structure. Copper (11) halide complexes of some substituted pyridine-N-oxides have been studied[51, 52] and have been reported as binuclear on the basis of the copper acetate type magnetic behaviour.

Halogen Bridged Complexes

The dimeric structures of $LiCuCl_3.2H_2O$[53], $KCuCl_3$ and NH_4CuCl_2[54] have been confirmed by X-ray analysis. The structure of $KCuCl_3$ is shown in figure 11a. The compound $KCuCl_3$ has a maximum at about 30°K in the susceptibility versus temperature curve: this is indicative of antiferromagnetism. The room temperature magnetic moment of 1.77 B.M.

FIGURE 11. STRUCTURE OF HALOGEN BRIDGED COPPER(11) COMPLEXES.

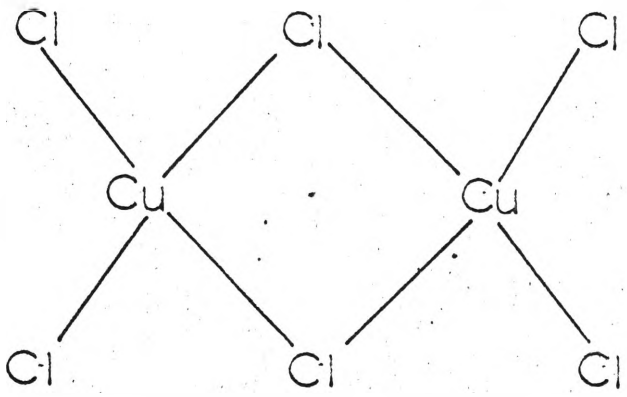
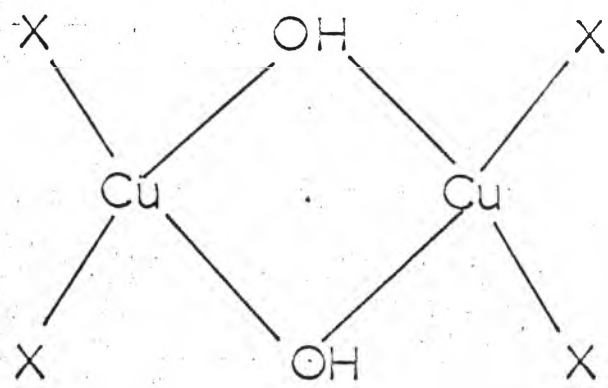


FIGURE 12. STRUCTURE OF HYDROXYL BRIDGED COPPER(11) COMPLEXES.



In fields of the order of 10,000 oersted

$\frac{H}{kT} \simeq 0.7T$ and since $\sinh x \simeq x$ for $x < 0.1$,

equation (13) simplifies to

$$M = \frac{N\mu^2 H}{kT} \left\{ \exp\left\{ \frac{-4J}{kT} \right\} + \left\{ \frac{\mu H}{kT} \right\}^2 \right\}^{-\frac{1}{2}}$$

for $T > 7^\circ K$

Therefore,

$$\chi = \frac{M}{H} = \frac{N\mu^2}{kT} \left\{ \exp\left\{ \frac{-4J}{kT} \right\} + \left\{ \frac{\mu H}{kT} \right\}^2 \right\}^{-\frac{1}{2}} \quad \ldots\ldots\ldots (14)$$

Crystallographic structure determinations [61, 62] have shown that both copper (11) chloride and copper (11) bromide contain infinite linear halogen bridged chains of copper atoms. It was found that the distances between chains are appreciably larger than the distance between copper atoms within a chain. Adjacent copper atoms are linked together along the chain by two bridging halogen atoms. Barraclough and Ng[59] contended that the copper-copper distance was too large for direct interaction and therefore they assumed that the exchange operates through bridging atoms. Good agreement was obtained by substituting the values of $g = 2.20$, $Tc = 70^\circ K$ for $CuCl_2$ and $g = 2.13$, $Tc = 226^\circ K$ for $CuBr_2$. The experimental results obtained[59] are shown, together with the theoretical curves for $CuCl_2$ and $CuBr_2$ in figure 12a. Recently, Dubicki et al[25] have studied the magnetic behaviour of copper (11) oxalate and found that it could be explained satisfactorily by the Barraclough and Ng[59]

equation. It was thought[25] that the exchange mechanism for spin coupling involves the delocalised π cloud of the bridging oxalate ions[70] although direct spin-spin interaction is possible[2].

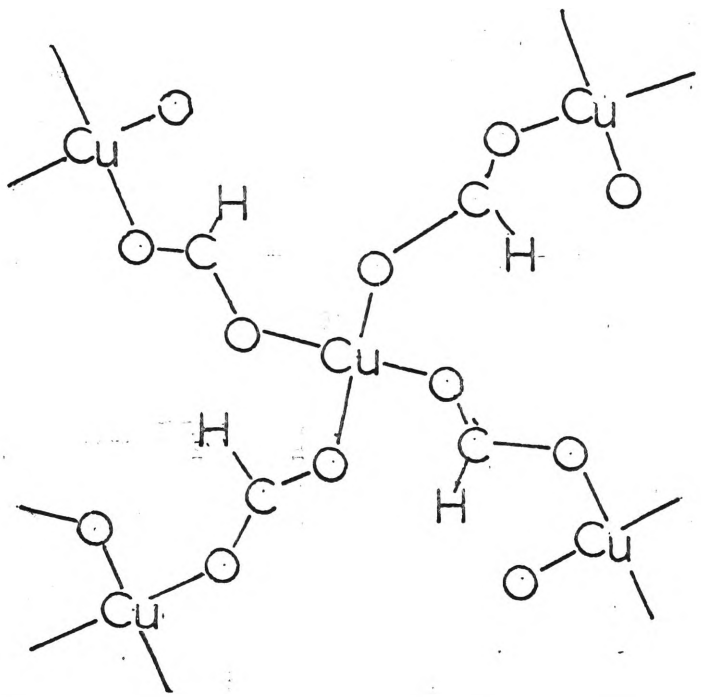
Hydroxyl Bridged Complexes

Several workers[63-68] have prepared compounds which have antiferromagnetic characteristics. The antiferromagnetic behaviour is attributed to superexchange through bridging hydroxyl ions in binuclear complexes (figure 12b).

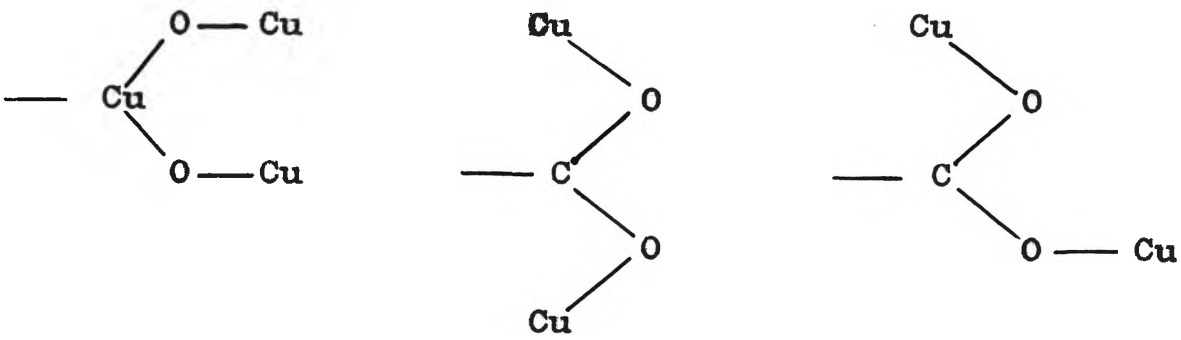
Copper (11) Complexes with more than One Bridging Atom
Copper (11) Formate

Copper (11) formate appears in a variety of modifications, of which some have been characterised by X-ray diffraction. Kirijama[69] has studied copper (11) formate tetraformate. Martin[70] discussed the subnormal magnetic moment (1.64 B.M.) of the tetrahydrate in terms of superexchange through a low energy π - pathway from the 3 d_{yz} and 3 d_{zx} orbitals of the copper (11) ions and the 2 p_{π} orbital of the connecting formate group (figure 13). Martin and Waterman[70] suggested that a $3d_{yz}$ or $3d_{xz}$ electron should be promoted to the $3d_{x^2-y^2}$ orbital so that a π path can be available. From calculations[71] and experimental[72] results for the copper (11) alkanates, energy of about 21,000 - 27,000 cm^{-1} would be required. They preferred the π path to the σ path considering that the 'preconditioning' of the π path is energetically easier. Martin and Waterman[70] suggested

FIGURE 13. Structure of Copper(11) Formate Polymer



three possible bridging arrangements:



Syn-Syn (a) Anti-Anti (b) Anti-Syn (c)

The syn-syn arrangement leads to copper (11)-copper (11) interaction similar to that of copper (11) acetate monohydrate. The anti-anti arrangement shown in (b) also leads to exchange demagnetisation observed in copper (11) formate tetrahydrate. The large copper-copper distance of 5.6Å within a layer as well as the interlayer distance of 6.2Å precludes direct copper-copper interaction. The observed antiferromagnetic exchange interaction was, therefore, ascribed to superexchange. Similar behaviour has been observed[24] on copper (11) formate tetraformic acid (μ = 1.61 B.M). The anti-syn bond arrangement (c) has been established for the royal blue isomer of copper (11) formate. The anti-syn bond arrangement does not appear to provide a pathway for antiferromagnetic exchange interaction since the royal blue isomer is magnetically normal (μ = 1.90 B.M.). Similar magnetic behaviour and structures have been reported for bis

salicylaldehyde copper (11)[73] (μ = 1.86 B.M.), N, N^1 - Disalecylideneethylenediamine copper (11)[74-75] (μ = 2.04 B.M.) and N, N^1 - Disalicylidenepropane - 1, 2 - diamine copper (11) monohydrate (μ = 1.86 B.M.[76]) and its anhydrous form (μ = 1.77 B.M.[77]) and are related to copper (11) formate behaviour by virtue of anti-syn bridging bond arrangements over two or more $copper^{2+}$ atoms.

Copper (11) Benzoate

The X-ray structural analysis of copper (11) benzoate trihydrate has been carried out by Koisumi[22, 78]. Inoue[22, 23] prepared the compound for X-ray analysis and found that it had a magnetic moment of 1.87 B.M. and that it obeyed the Curie Law. They attributed this normal magnetic moment to the large copper-copper distance (3.15Å) compared to 2.56Å in copper acetate[39, 40], and more in particular to the unfavorable orientation of 3d orbitals on adjacent copper (11) ions which does not appear to give an effective overlap for direct copper-copper interaction[22, 23].

The crystal structure of $CuCl_2$ (1, 2, 4 - triazole) is very similar to that of copper (11) benzoate trihydrate. Two nitrogen atoms of the triazole molecule replace the two oxygens of the carboxylate group. Chloride ion bridges are formed instead of water bridges. The normal magnetic moment of this compound of 1.81 B.M. is expected from its structure[22], $CuSO_4$. 1, 2, 4 triazole. $4H_2O$ was

shown to have a magnetic moment of 1.62 B.M. Two modifications of bis (triazolate) copper (11) complex have been prepared, the magnetic moments of which are 1.4 and 1.66 B.M. respectively.[23]

Copper (11) Compounds with Substituted Benzoquinone

Kobayaski et al[80, 81] have measured the magnetic susceptibilities of 2, 5 - dihydroxy-p-benzoquinone copper (11) as well as the dichloro - and dibromo - complexes at low temperatures. On the basis of the structure of the ligand, the copper-copper distance was assumed to be about 7.5Å (figure 14). The observed exchange interaction of J = 10-17 cm^{-1} was therefore explained in terms of superexchange. They found that the magnetic behaviour was influenced only slightly by chloride and bromine substituents in the aromatic ring.

Discussing the magnetic behaviour of these compounds, Kobayaski et al[81] have taken into consideration the end effect, i.e. the effect of terminal copper atoms in the chain structure and the presence of either an even or an odd number of spins in the chain. They assumed that the spins at the ends of the chains are under smaller influence from the field than the spins in the middle of the chain, and that, therefore, paramagnetic susceptibilities observed at lower temperatures may be due to this effect. The odd number effect will also give a paramagnetic susceptibility at low temperatures. When the number of the spins is two,

STRUCTURE OF 2,5 DISUBSTITUTED -P- BENZOQUINONE

COPPER(11).

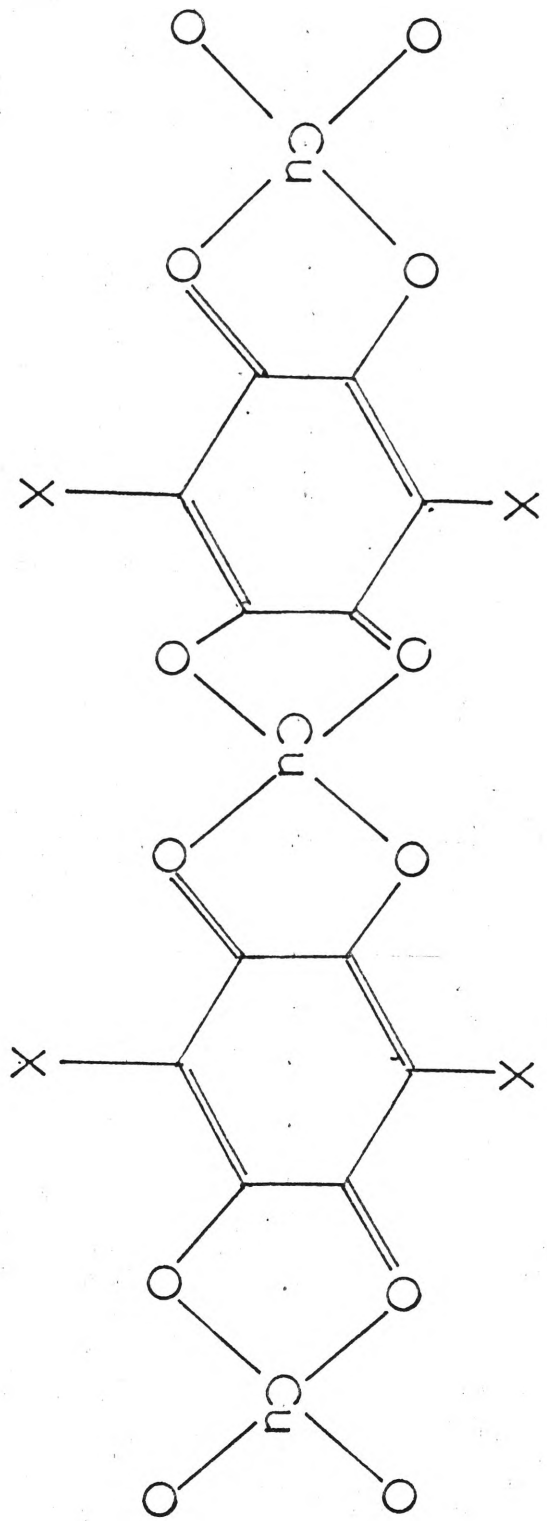


FIGURE 14.

in the case of antiferromagnetic coupling, the ground level is occupied by the paired spins and is not magnetic[81].

The theoretical magnetic susceptibility of an infinite one dimensional lattice of Ising's spins is expressed in terms of exchange coupling constant J between nearest neighbours.

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \exp(J/kT)$$

where N = Avagadro's number

g = spectroscopic splitting factor

β = Bohr Magnetons and

k = Boltzmann's constant

By subtracting magnetic behaviour due to the end effect, the curve agrees with the theoretical curve, J = k(-24°K). Magnetic susceptibilities of one-dimensional lattices using Heinsberg's spin model for spins from 2 to 10 has been exactly calculated by Griffiths[82]. When the number of spins in a chain is odd, the magnetic susceptibility shows an apparent paramagnetic increase at very low temperatures. On the other hand, when the number of spins in the chain is even, the magnetic susceptibility vanishes with decreasing temperatures. The coupling constant J of 2, 5 - Dihydroxy-p-benzoquinonato copper (11) was estimated at about k(-24°K) on the basis of the Ising's spin model and about K(-14°K) on the basis of Heisenberg's spin model with the results used by Griffiths.

3.0 DISCUSSION:

3.1 THE COPPER (11) COMPLEXES OF ∝-ACYLOIN OXIMES

In this section are discussed the copper (11) complexes of ∝-benzoin oxime, ∝-methylbenzoin oxime, ∝-phenylbenzoin oxime and ∝-furoin oxime.

The purpose of preparing and investigating these compounds was to determine whether the substituted ligands gave structures which allowed antiferromagnetic exchange to take place within the molecule similar to that described by Kokot[91] for ∝-benzoin oxime copper (11).

It was considered that the magnetic behaviour of the polymer, ∝-benzoin oxime copper (11), might be explained if a similar treatment was applied to that used by Kobayashi et al[81] in explaining the magnetic behaviour of the copper (11) benzoquinones.

Experimental data for the temperature variation of the susceptibility (table 9), the room temperature magnetic moment (table 8), the elemental analysis (table 6) and the general physical properties (table 7), are listed at the end of this section.

Alpha benzoin oxime was shown by Feigl[92] to be a good analytical reagent for copper (11) ions. Since the acyloin complex was insoluble in ammonium hydroxide, Feigl et al[93] proposed an inner complex structure in which the oxime was regarded as being dibasic. In 1955, Suter

and West[94] investigated the solubility of ∝-acyloin oxime copper (11) complexes in a series of organic amines. They found that the behaviour of the copper (11) salts of acyloin oximes can best be interpreted by assuming a polymeric structure for these compounds. They proposed the structure shown in figure 15a.

The room temperature magnetic moment of 1.22 B.M. at 22.6°C of ∝-benzoin oxime copper (11) in this work compares favorably with the moment of 1.18 B.M. obtained by Kokot. Kokot investigated the variation in the magnetic susceptibility of ∝-benzoin oxime copper (11) due to temperature and found a very steep initial rise in the reciprocal of the magnetic susceptibility below the maximum at approximately 200°K. He concluded that the magnetic behaviour represents a temperature dependent equilibrium between magnetically stronger excited levels and magnetically weaker ground levels as opposed to the equilibrium in copper (11) acetate in which the lower level is diamagnetic. Kokot[24] proposed two possible polymeric structures for this compound, one of which he suggested was more feasible and in fact, this structure shown in figure 15a is identical to that postulated independently by Suter and West[94]. This structure contains an infinite linear chain of contiguous copper atoms linked by oxygen and N = O bridges. Exchange through the oxygen bridges is probably responsible for the observed antiferromagnetism.

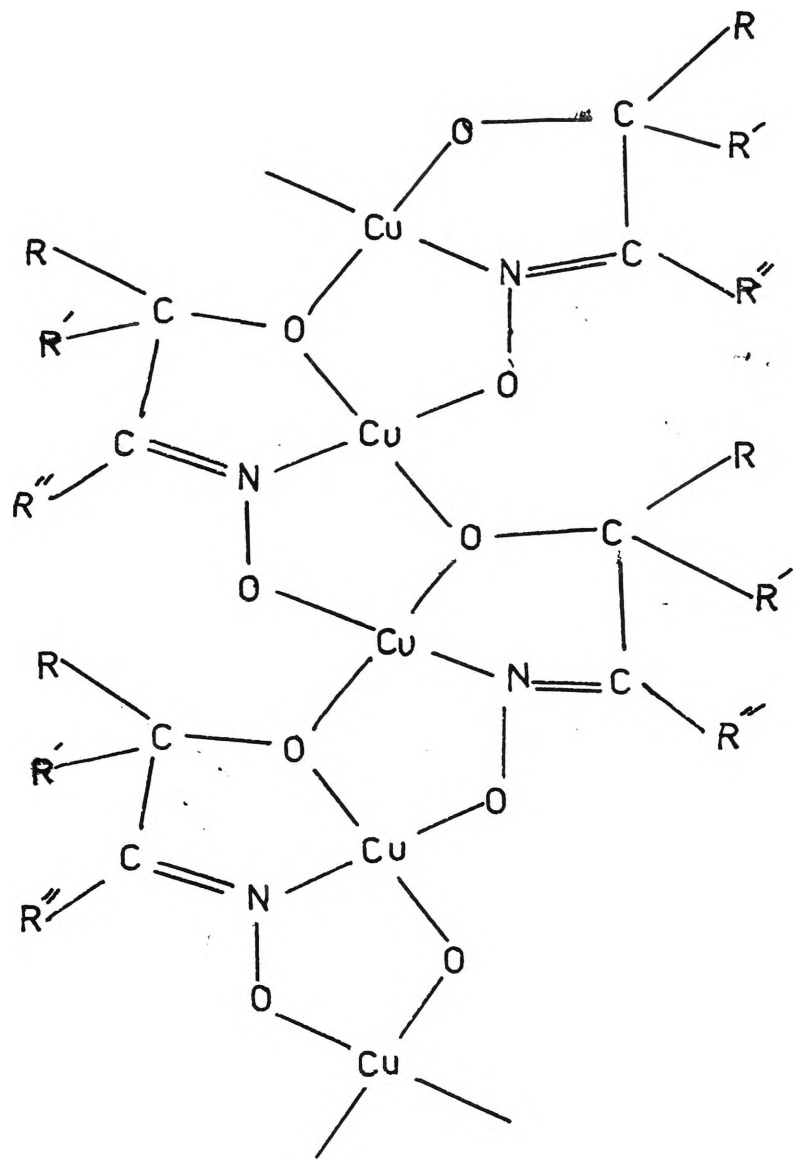
The other structure shown in figure 15b was dismissed on the grounds that exchange interaction would be confined to isolated pairs of copper atoms and thus should give rise to copper (11) acetate type of magnetic behaviour.

In addition to the α-benzoin oxime copper (11) complex, three other acyloin oxime copper (11) complexes were studied in this work. They are α-methylbenzoin oxime copper (11), α-phenylbenzoin oxime copper (11) and α-furoin oxime copper (11) for which magnetic moments of 1.22 B.M., 1.20 B.M., and 1.21 B.M. respectively were obtained (table 8). The subnormal magnetic moments indicate that all four compounds have structures which allow antiferromagnetic exchange to take place. The effect of substituents in the molecule appears to be negligible and there is no variation between the room temperature moments. Furthermore, the susceptibility versus temperature curves shown in figure 16 are very similar and $J = 435\ cm^{-1}$ is the same for all compounds in this series. The experimental magnetic moments at different temperatures are shown in figure 17 for this series of compounds.

The polymeric nature of the compounds studied in this work is also reflected, in addition to the magnetic behaviour, in the 1 : 1 ratio of ligand to copper in the complexes (table 6), in their behaviour towards thermal decomposition (table 7) and in their poor solubility

FIGURE 15 a.

∝-ACYLOIN OXIME COPPER(11).

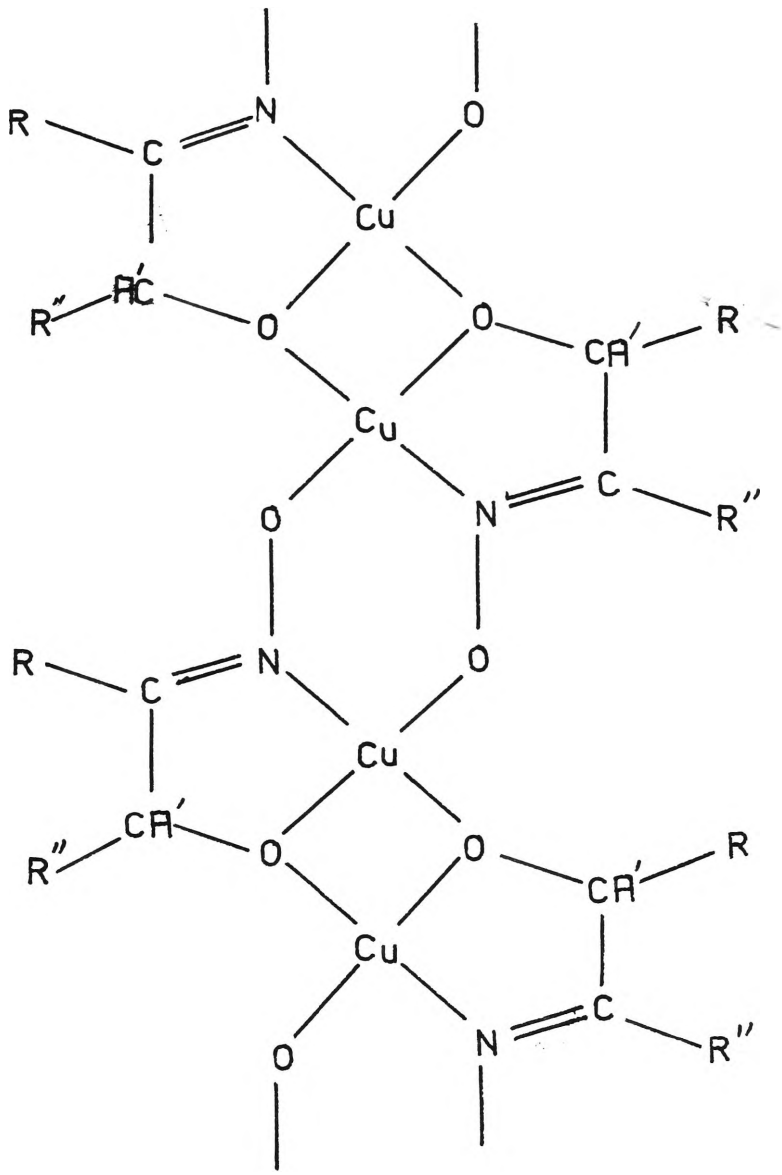


where R and R" $=-C_6H_5$ and R' $=-H, -CH_3$, or $-C_6H_5$

and where R and R" $=-C_4H_4O$ and R' $=-H$.

FIGURE 15 b.

oC-ACYLOIN OXIME COPPER(11).



where R and R" $=-C_6H_5$ and R' $=-H, -CH_3$ or $-C_6H_5$

and where R and R" $=-C_4H_4O$ and R' $=-H$.

in the more common solvents (table 7).

In this work, X-ray techniques were unavailable and therefore the approximate sizes of the molecules were not known. However, using the Kobayashi procedure, it was considered that if one were to add the magnetic susceptibility resulting from the end effect and the odd-even effect to the magnetic susceptibility resulting from the interacting copper (11) atoms, as described by equation 15, in the correct ratio, the resulting theoretical curve should, if these assumptions are correct, correspond to the experimental χ versus T curves. It was possible to fit theoretical curves to the complex experimental susceptibility versus temperature data by adding 12.5 percentum Curie Law behaviour to the χ versus T curve obtained from equation 15 using the values for g and J shown in table 5. The results are shown in table 9.

The good fit of the theoretical curve based on equation 15 derived for an infinite linear chain of interacting copper (11) atoms indicates the feasibility of the suggested general structure in figure 16a. This structure is virtually identical with that proposed for α-benzoin oxime by Kokot[91] and by Suter and West[94]. It involves infinite linear chains of copper (11) atoms linked by O and N = O bridges which may permit antiferromagnetic exchange interaction.

The part of the susceptibility due to the odd-even spin

number effect expected by Kobayashi et al[81] at low temperatures is included with the end group effect since neither effect can be estimated separately. Any given sample will contain varying proportions of molecules of both even or odd numbers of paramagnetic atoms in the chain. In addition to this, any sample will contain molecules of somewhat differing chain lengths. The latter is unlikely to result in any significant errors provided the chain length is sufficient to permit interaction between a large enough number of paramagnetic atoms to approximate the magnetic behaviour described by equation (15). The excellent agreement between theoretical and experimental curves justifies the adopted procedure.

TABLE 5

Theoretical Tc, g and J Values for Acyloin Oxime Copper (11) Complexes

Compound	Tc°K	g	J (cm^{-1})
$(C_{14}H_7NO_2)Cu$	396.5	2.11	547
$(C_{15}H_{14}NO_2)Cu$	396.5	2.11	547
$(C_{20}H_{16}NO_2)Cu$	396.5	2.11	547
$(C_{10}H_{11}NO_4)Cu$	396.5	2.14	547

The magnetic susceptibility of these compounds is derived from:

	Percentum
Curie Law Contribution	12.5
- Terminal Copper Atoms plus Odd-Even Effect plus Effect of varying Chain Length	
Contribution from Interacting Copper Atoms in the middle of the chains as described by equation (15)	87.5

Using equation (14) derived by Barraclough and Ng[59], it was found that the agreement with the experimental curves was not as good as with equation (15). It has since been intimated that the Barraclough equation may be incorrect[91].

FIGURE 16

MAGNETIC SUSCEPTIBILITY AT DIFFERENT TEMPERATURES OF COPPER(11) COMPLEXES OF ∝-ACYLOIN OXIMES.

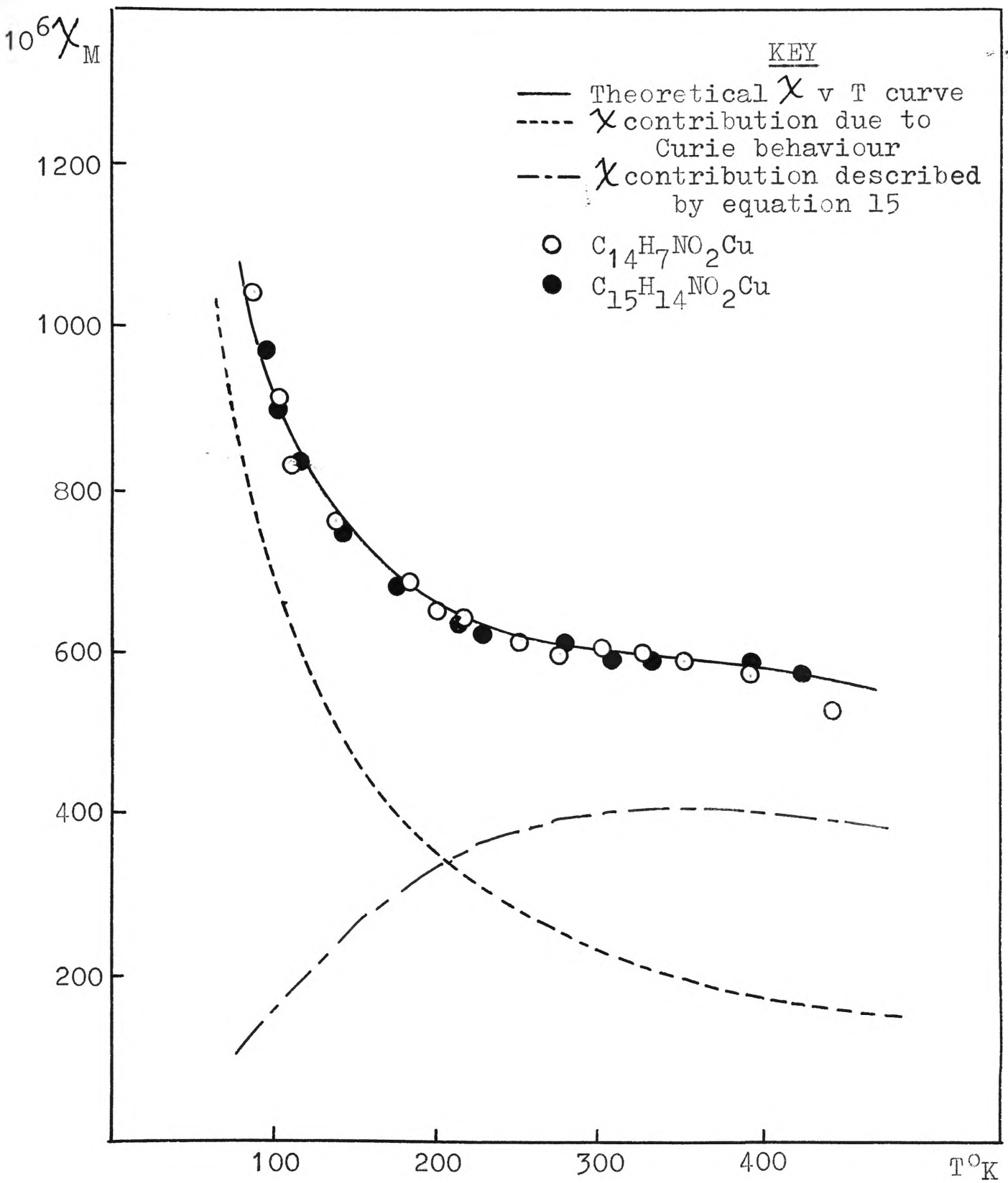


FIGURE 16 (cont.)

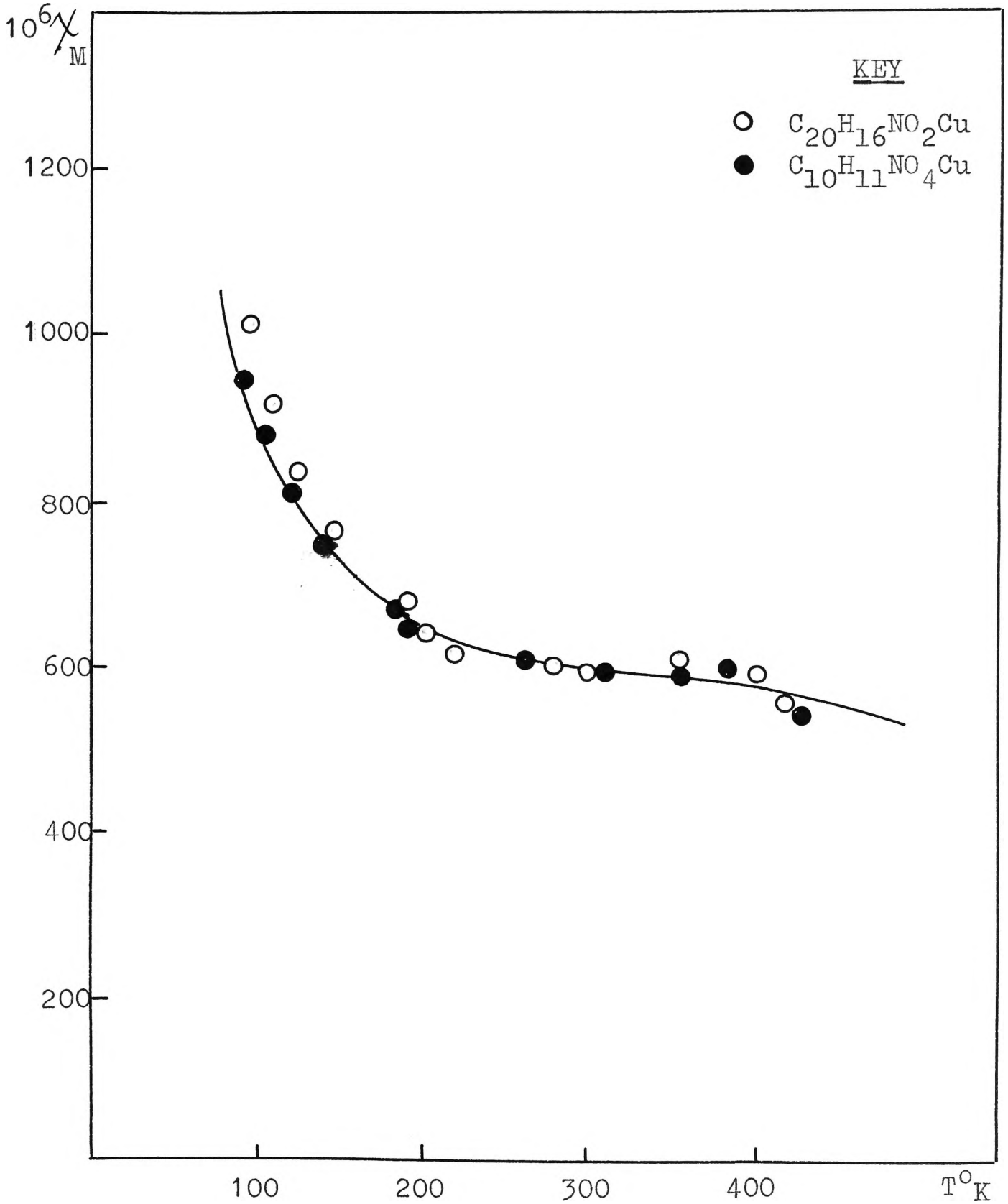
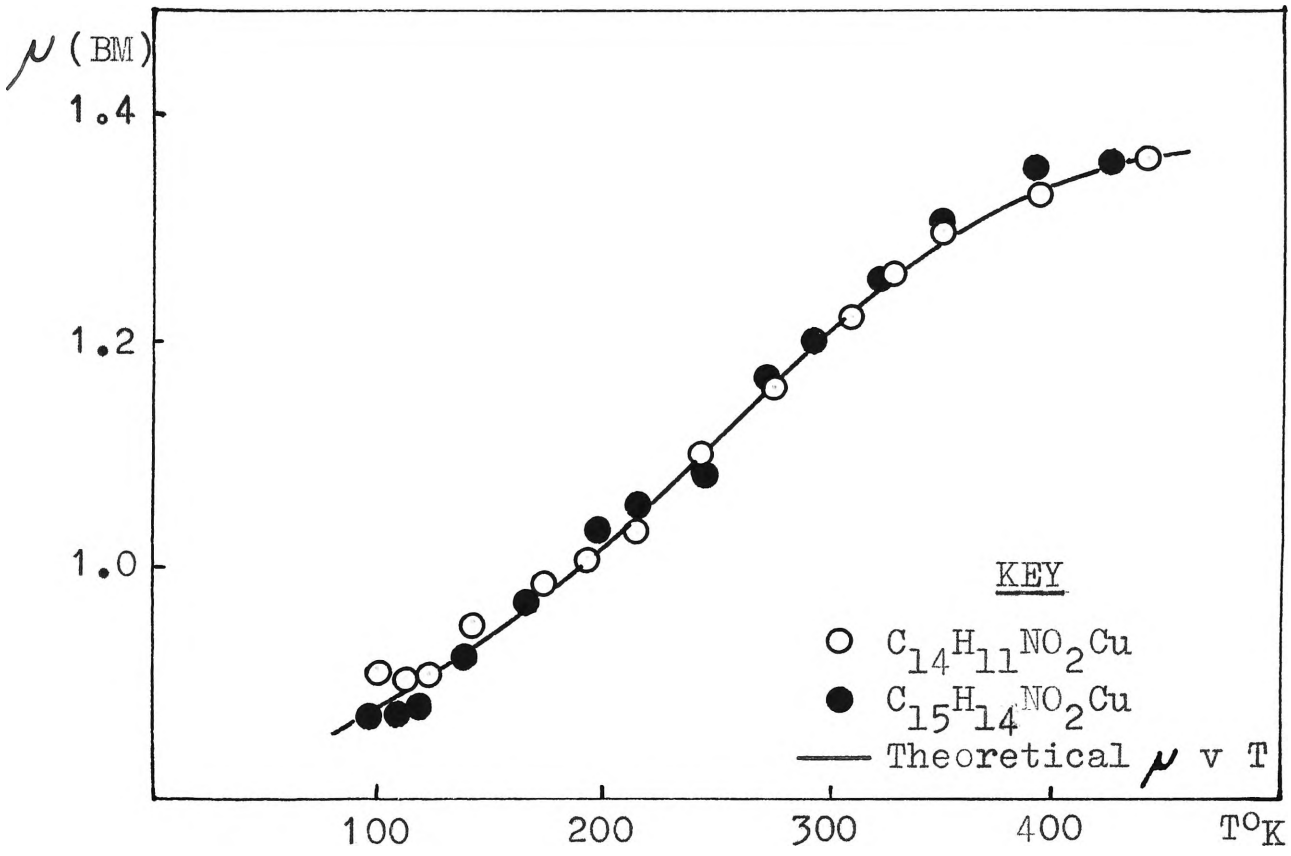


FIGURE 17.

MAGNETIC MOMENTS AT DIFFERENT TEMPERATURES OF COPPER(11) COMPLEXES OF ∝-ACYLOIN OXIMES.



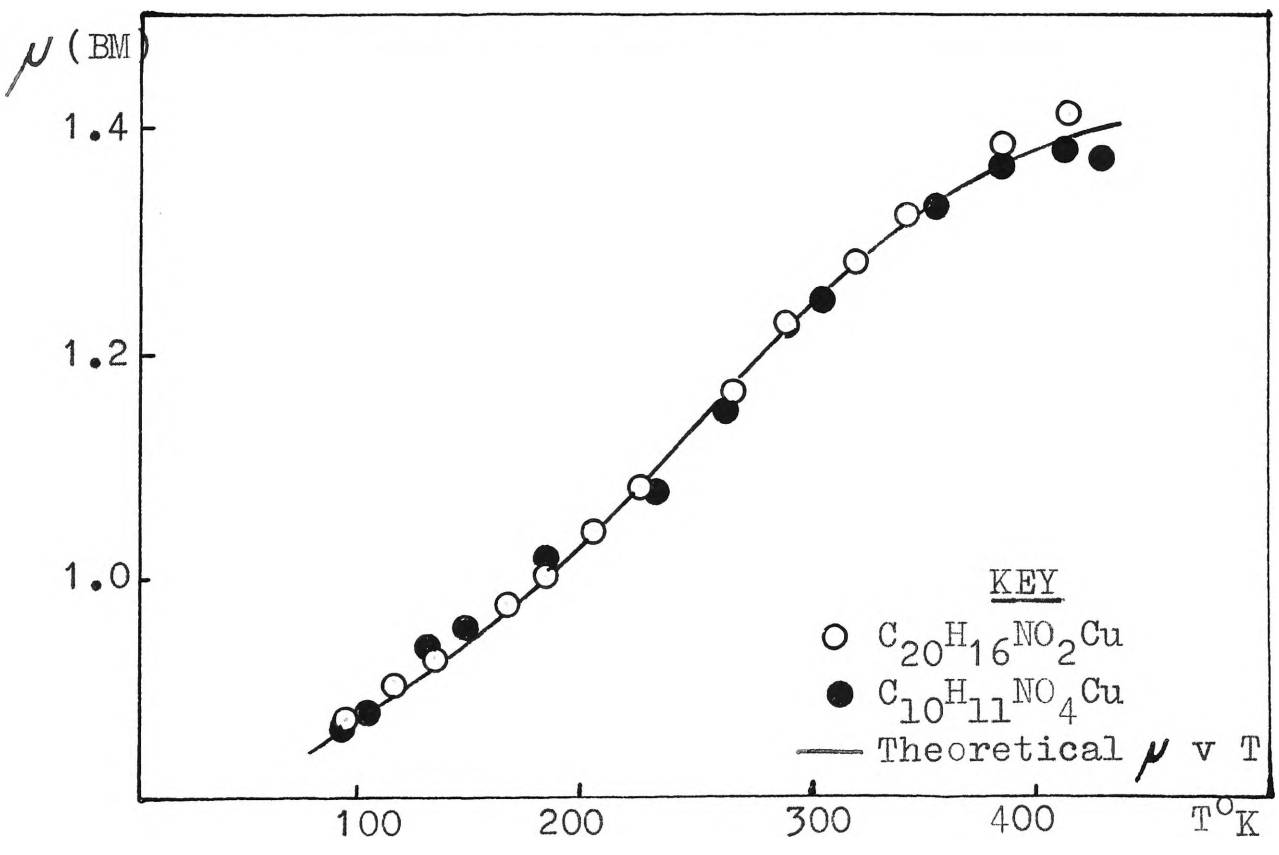


TABLE 6

ELEMENTAL ANALYSIS OF COPPER (11) COMPLEXES OF ∝-ACYLOIN OXIMES

	COMPOUND	FORMULA	C		H		N		O		Cu	
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1.	∝-Benzoin Oxime Copper (11)	$(C_{14}H_{11}NO_2)Cu$	58.6	58.3	3.9	3.8	4.7	4.9	10.8	11.1	21.9	22.0
2.	∝-Methylbenzoin Oxime Copper (11)	$(C_{15}H_{14}NO_2)Cu$	59.6	59.3	4.1	4.6	5.0	4.6	11.1	10.5	20.9	20.9
3.	∝-Phenylbenzoin Oxime Copper (11)	$(C_{20}H_{16}NO_2)Cu$	65.5	65.7	4.3	4.4	3.5	3.8	8.6	8.8	17.1	17.4
4.	∝-Furoin Oxime Copper (11)	$(C_{10}H_7NO_4)Cu$	44.7	44.8	2.4	2.6	5.8	5.3	23.2	23.8	23.5	23.7

TABLE 7

PHYSICAL PROPERTIES OF COPPER (11) COMPLEXES OF ∝-ACYLOIN OXIMES

	COMPOUND	COLOUR	BEHAVIOUR ON HEATING	Water	Acetone	Isopropyl Alcohol	Chloroform	Ether	Ammonia	0.1N Hcl
1.	$(C_{14}H_{11}NO_2)Cu$	Green	Darkens to Black Residue. Decomposes above 285°C	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble on Heating to give a colourless solution.
2.	$(C_{15}H_{14}NO_2)Cu$	Green	" "	"	"	"	"	"	"	" "
3.	$(C_{20}H_{16}NO_2)Cu$	Green	" "	"	"	"	"	"	"	" "
4.	$(C_{10}H_{11}NO_4)Cu$	Very pale Blue	" "	"	"	"	"	"	"	" "

TABLE 8

MAGNETIC DATA AT ROOM TEMPERATURE FOR -ACYLOIN OXIME COPPER (11) COMPLEXES

	COMPOUND	T°C	$10^6\chi_g$	$10^6\chi_M$	$-10^6\Delta$	$10^6\chi_M^1$	μ B.M.
1.	$(C_{14}H_7NO_2)Cu$	22.6	2.10	400	207.8	608	1.22
2.	$(C_{15}H_{14}NO_2)Cu$	24.8	2.01	409	200.6	609	1.21
3.	$(C_{20}H_{16}NO_2)Cu$	21.7	1.70	388	233.9	622	1.22
4.	$(C_{..}H_{..}NO_{..})Cu$	22.1	2.30	460	157.2	617	1.20

TABLE 9

Experimental gram, molar susceptibilities and magnetic moments at different temperatures for Copper (11) complexes of α-acyloin oximes.

1. α-Benzoin Oxime Copper (11) - $(C_{14}H_{11}NO_2)Cu$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_M$	μ (B.M.)
98.0	3.60	1041	0.91
109.7	3.16	915	0.90
120.0	2.96	857	0.91
140.5	2.73	790	0.95
169.8	2.46	710	0.99
193.3	2.28	658	1.01
214.9	2.22	643	1.03
244.5	2.11	610	1.10
274.3	2.10	608	1.16
300.8	2.10	608	1.22
326.2	2.09	604	1.26
347.5	2.07	598	1.30
390.0	1.98	572	1.34
438.7	1.80	521	1.36

TABLE 9 (Continued)

2. α-Methylbenzoin Oxime Copper (11) - $C_{15}H_{14}NO_2)Cu$

T°K	$10^6\chi_g$	$10^6\chi_M$	μ(B.M.)
97.6	3.13	950	0.87
110.4	2.84	861	0.87
118.9	2.64	800	0.87
139.6	2.47	750	0.92
167.4	2.31	702	0.97
197.8	2.25	681	1.04
214.8	2.15	652	1.06
245.4	2.09	633	1.10
274.6	2.04	620	1.17
297.8	2.01	609	1.21
324.2	2.05	623	1.27
350.6	2.02	613	1.32
392.7	1.95	591	1.37
430.8	1.60	486	1.30

TABLE 9 (Continued)

3. α-Phenylbenzoin Oxime Copper (11) - $(C_{20}H_{16}NO_2)Cu$

T°K	$10^6\chi_g$	$10^6\chi_M$	μ(B.M.)
97.6	2.79	1019	0.87
109.4	2.55	930	0.91
119.4	2.31	843	0.90
137.6	2.15	769	0.92
169.3	1.86	681	0.97
190.4	1.75	640	0.99
210.9	1.70	620	1.03
230.8	1.69	618	1.07
270.6	1.70	622	1.16
294.7	1.70	622	1.22
325.4	1.69	618	1.27
347.7	1.68	613	1.31
388.6	1.65	604	1.38
419.2	1.59	581	1.40

TABLE 9 (Continued)

4. α-Furoin Oxime Copper (11) - $(C_{10}H_{11}NO_4)Cu$

T^oK	$10^6\chi_g$	$10^6\chi_M$	μ(B.M.)
96.1	3.53	949	0.86
104.9	3.34	899	0.87
132.4	3.02	813	0.93
150.0	2.78	748	0.95
184.7	2.53	679	1.01
203.9	2.38	639	1.03
230.0	2.28	612	1.07
264.0	2.28	612	1.14
309.7	2.31	620	1.24
356.8	2.29	616	1.33
384.4	2.21	595	1.36
414.4	2.09	561	1.37
430.7	1.98	532	1.36

3.2 BIDENTATE COPPER (11) COMPLEXES OF IMIDAZOLE, BENZIMIDAZOLE, BENZOTRIAZOLE[98] AND SUBSTITUTED BENZIMIDAZOLE.

Independent investigations carried out by the author on organic compounds capable of inhibiting the corrosion of metallic copper led to the preparation of a wide range of bi-, tri- and quadridentate derivatives of benzotriazole. The purpose of investigating the magnetic behaviour of the copper (11) complexes of these derivatives was to determine whether the structures were of a polymeric nature and whether the compounds exhibited antiferromagnetic exchange interaction similar to the α-acyloin oxime complexes of copper (11) described in the previous section.

On the basis of elemental analysis, compounds other than benzotriazole copper (11) chloride and benzotriazole copper (11) hydroxide, discussed in this section, correspond to an empirical formula LCuCl where L is imidazole, benzimidazole and 2-methyl, 2-ethyl, 2-vinyl, 2-propyl, 2-butyl, 2-pentyl, 2-decyl, 2-stearyl, 2-phenyl, 2-naphthyl, 2-benzyl, 2-α-aminoethyl, 2-α-hydroxyethyl, and 2-α-mercapto-benzimidazole. A general formula of $L_3Cu_2X_2$ was found to satisfy the requirements of the elemental analysis of benzotriazole copper (11) chloride and benzotriazole copper (11) hydroxide.

Experimental data for the temperature variation of the susceptibility, the room temperature magnetic moments, the

elemental analysis and the physical properties of this series of compounds are listed in tables 11, 12, 13 and 14 respectively at the end of the section.

The room temperature magnetic moment of imidazole copper (11) chloride is 1.60 B.M. The copper (11) complexes of benzimidazole and substituted benzimidazoles have room temperature magnetic moments which fall in the range 1.25 to 1.40 B.M. The complexes benzotriazole copper (11) chloride and benzotriazole copper (11) hydroxide have room temperature magnetic moments of 1.56 B.M. and 1.54 B.M. respectively. These results indicate that the addition of the fused benzene ring to the imidazole ring appears to alter the electronic configuration of the imidazole ring in such a way as to facilitate superexchange. The replacement of hydrogen by alkyl and aryl radicles in the two position of benzimidazole appears to have little or no effect on the magnetic behaviour of the compound.

As shown in figure 18, the experimental temperature variation of the susceptibility could be reproduced theoretically using the same procedure as described in the previous section (3.1). The constants used in equation 15 are listed in table 10. The experimental magnetic moments at different temperatures are shown in figure 19. The deviations at higher temperatures could be due to the average chain length falling short of the number of interacting atoms required to satisfy entirely the conditions of equation 15.

TABLE 10

THEORETICAL Tc, g and J VALUES FOR IMIDAZOLE, BENZIMIDAZOLE, BENZOTRIAZOLE AND SUBSTITUTED BENZIMIDAZOLE COPPER (11) COMPLEXES.

	COMPOUND	Tc °K	g	J cm^{-1}
1.	$C_3H_3N_2CuCl$	160	2.18	221
2.	$C_7H_5N_2CuCl$	315	2.18	435
3.	$C_8H_7N_2CuCl$	315	2.25	435
4.	$C_9H_7N_2CuCl$	315	2.18	435
5.	$C_9H_9N_2CuCl$	315	2.25	435
6.	$C_{10}H_{11}N_2CuCl$	315	2.25	435
7.	$C_{11}H_{13}N_2CuCl$	315	2.25	435
8.	$C_{12}H_{15}N_2CuCl$	315	2.25	435
9.	$C_{17}H_{25}N_2CuCl$	315	2.25	435
10.	$C_{24}H_{39}N_2CuCl$	315	2.25	435
11.	$C_{13}H_9N_2CuCl$	315	2.25	435
12.	$C_{14}H_{11}N_2CuCl$	315	2.25	435
13.	$C_{17}H_{12}N_2CuCl$	315	2.25	435
14.	$C_9H_9N_2OCuCl$	315	2.05	435
15.	$C_9H_9N_2SCuCl$	315	2.05	435
16.	$C_9H_{10}N_3CuCl$	315	2.05	435
17.	$(C_6H_4N_3)_3Cu_2Cl_2$	261	2.11	360
18.	$(C_6H_4N_3)_3Cu_2(OH)_2$	261	2.11	360

For Imidazole Copper (11) chloride, a g value of 2.18 and a Tc of 160°K were substituted into equation 15 to give a J value of 221 cm^{-1}. For all members of the benzimidazole copper (11) chloride series, a spectroscopic splitting factor of 2.25 was used except in the cases of benzimidazole copper (11) chloride and 2-methylbenzimidazole copper (11) chloride. In all cases a Tc of 315°K was substituted into equation 15 to give a J value of 435 cm^{-1}. The stronger antiferromagnetic exchange interaction in benzimidazole copper (11) chloride compared to imidazole copper (11) chloride is also reflected in the lowering of Tc from 315°K to 160°K which appears to represent the influence of the fused benzene ring.

Figure 18 shows the theoretical χ versus T curves obtained by the procedure described in the previous section. In addition to the resultant theoretical curve, figure 18 shows the component parts representing the Curie Law behaviour and the curve obtained from equation 15 reflecting the linear antiferromagnetism along an infinite chain of bivalent copper atoms.

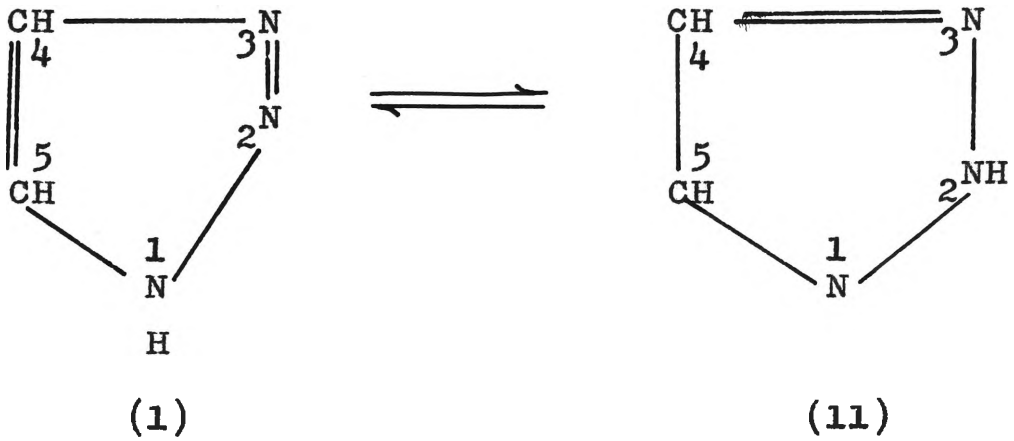
Imidazole copper (11) chloride requires ten percentum of terminal group and odd-even paramagnetism. The combined effect of these two contributing factors will be referred to as Curie behaviour. Benzimidazole copper (11) chloride and the substituted benzimidazole copper (11) chlorides required 12.5 percentum Curie behaviour. The larger amount

of Curie behaviour in benzimidazole complexes compared to imidazole copper (11) chloride may possibly be explained by the presence of electronic influences in benzimidazole copper (11) chloride which may lead to a lower degree of polymerisation compared to imidazole copper (11) chloride. As a consequence, there may be more end groups present in benzimidazole copper (11) chloride. This would lead to a higher percentage of Curie behaviour needed in the theoretical curve to produce 'a good fit' to the experimental data. The proposed structure in figure 20 is in agreement with the elemental analysis and the observed linear antiferromagnetism. The magnetic exchange interaction may utilize the Cu-Cl-Cu and or the Cu-L-Cu bridges in which L is the ligand containing the conjugated electronic system. The Cu-Cl-Cu system has been shown to exhibit antiferromagnetism by Barraclough and Ng[59]. However, as shown in a later section of this work, the magnetic behaviour of the quadridentate benzimidazole copper (11) complexes which do not involve chloride ions is virtually the same as that of the bidentate benzimidazole complexes. The similarity of the magnetic behaviour is apparent in similar values of the room temperature magnetic moments as well as the fact that the same values of $g = 2.25$, $J = 435\ cm^{-1}$ and 12.5 percentum Curie behaviour are required for both series of compounds. This may well indicate that the same bridging arrangement i.e. Cu-L-Cu, is responsible for the observed antiferromagnetic exchange demagnetisation in both cases.

For compounds containing the hydroxyl, amino and mercaptoethyl side groups, it appears that the groups in the side chain are not co-ordinated in the square plane of copper (11) atoms since the presence of one chloride ion per copper atom indicates that the ligands act as a monobasic acid. The postulated structure shown in figure 20 may permit exchange through chains of contiguous copper atoms via Cu-L-Cu and Cu-Cl-Cu bridges. Using equation 15 with g and Tc values as shown in table 10 and allowing for 12.5 percentum Curie Law, theoretical curves were produced which fitted the experimental data closely (figure 18) confirming that the compounds are polymeric antiferromagnets.

Benzotriazole copper (11) chloride and benzotriazole copper (11) hydroxide have, on the basis of elemental analysis, an empirical formula $L_3Cu_2X_2$ where L is benzotriazole and X is chloride or hydroxide. On the basis of the empirical formula, the copper appears to be, at first sight, in the 3+ oxidation state. However, this is highly improbable in view of the fact that in the course of preparation, no oxidising agents were present and in view of the well known difficulty of oxidising copper (11) to copper (111). It must therefore be assumed that one of the three ligand molecules acts as a neutral ligand.

Osotriazole exists in two tautomeric forms (1) and (11).



(1) (11)

Similar tautomeric forms may be postulated for benzotriazole

(1) (11)

The use of form (11) as a neutral ligand may explain the unusual empirical formula and permits the postulation of structure 21.

It is also possible to envisage bond formation of benzotriazole ~~of~~ To two copper atoms through nitrogen atoms (1) and (3) using tautomeric form (1) if it is assumed that the lone pair of electrons of N_1 are in an sp^2 hybridised orbital and the hydrogen atom bonded to the N_1 atom through an unhybridised $2p_z$ orbital. Even sp^3 hybridisation must not be entirely excluded as a possible solution.

Structure 21 permits antiferromagnetic exchange through contiguous chains of copper atoms via Cu-L-Cu bridges.

The higher proportion of Curie Law of 15 percentum compared to 12.5 percentum, for the other compounds of this series, with the exception of imidazole copper (11) chloride which has been discussed previously, supports this structure since the polymer is one dimensional. Using equation 15 with g and Tc values shown in figure 10, and allowing for the fiteen percentum Curie behaviour, theoretical curves were produced which fitted the experimental data closely, again confirming that the compounds are polymeric antiferromagnets.

FIGURE 18

MAGNETIC SUSCEPTIBILITIES AT DIFFERENT TEMPERATURES OF COPPER(11) COMPLEXES OF IMIDAZOLE, BENZIMIDAZOLE, BENZOTRIAZOLE AND SUBSTITUTED BENZIMIDAZOLES.

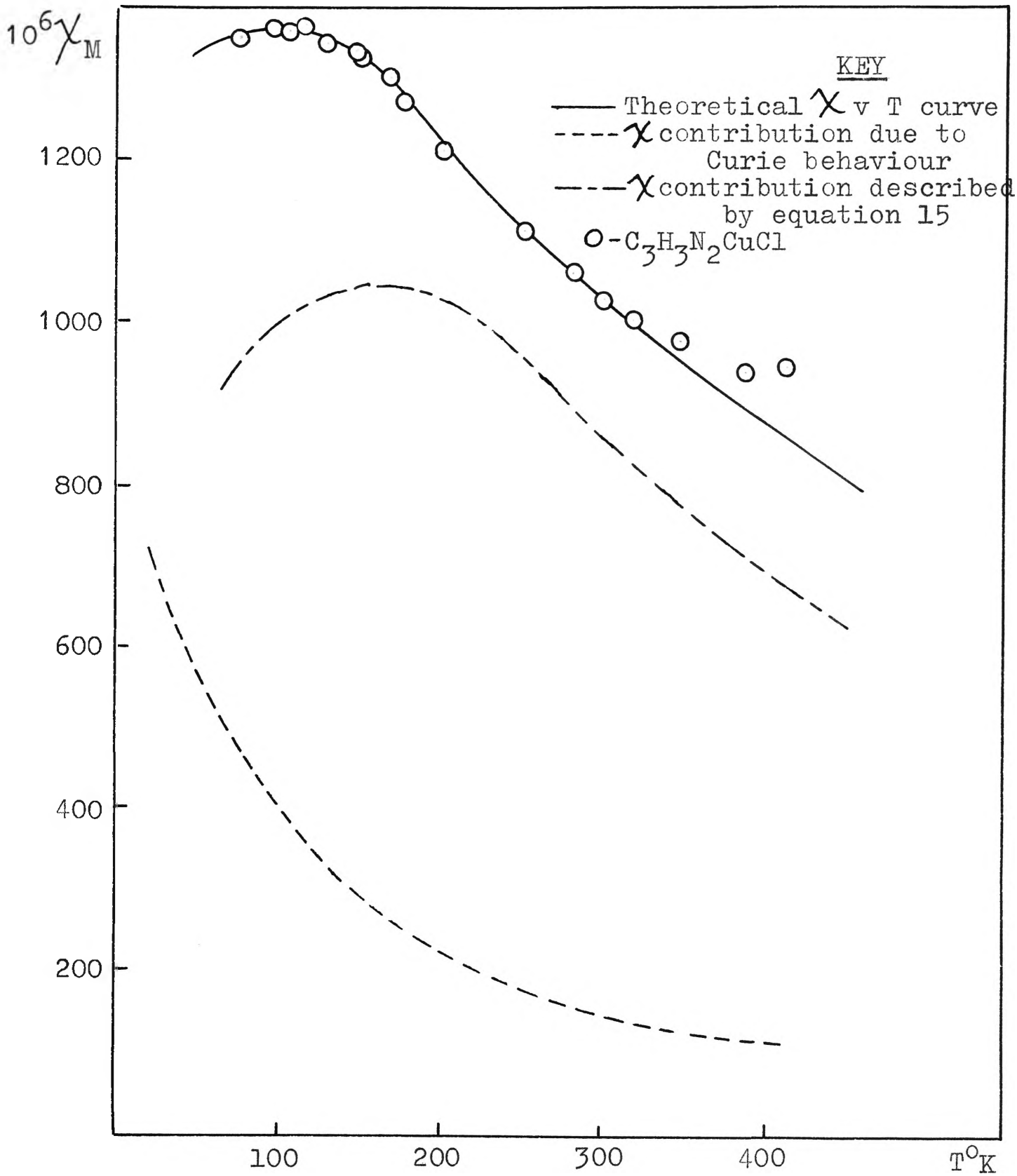
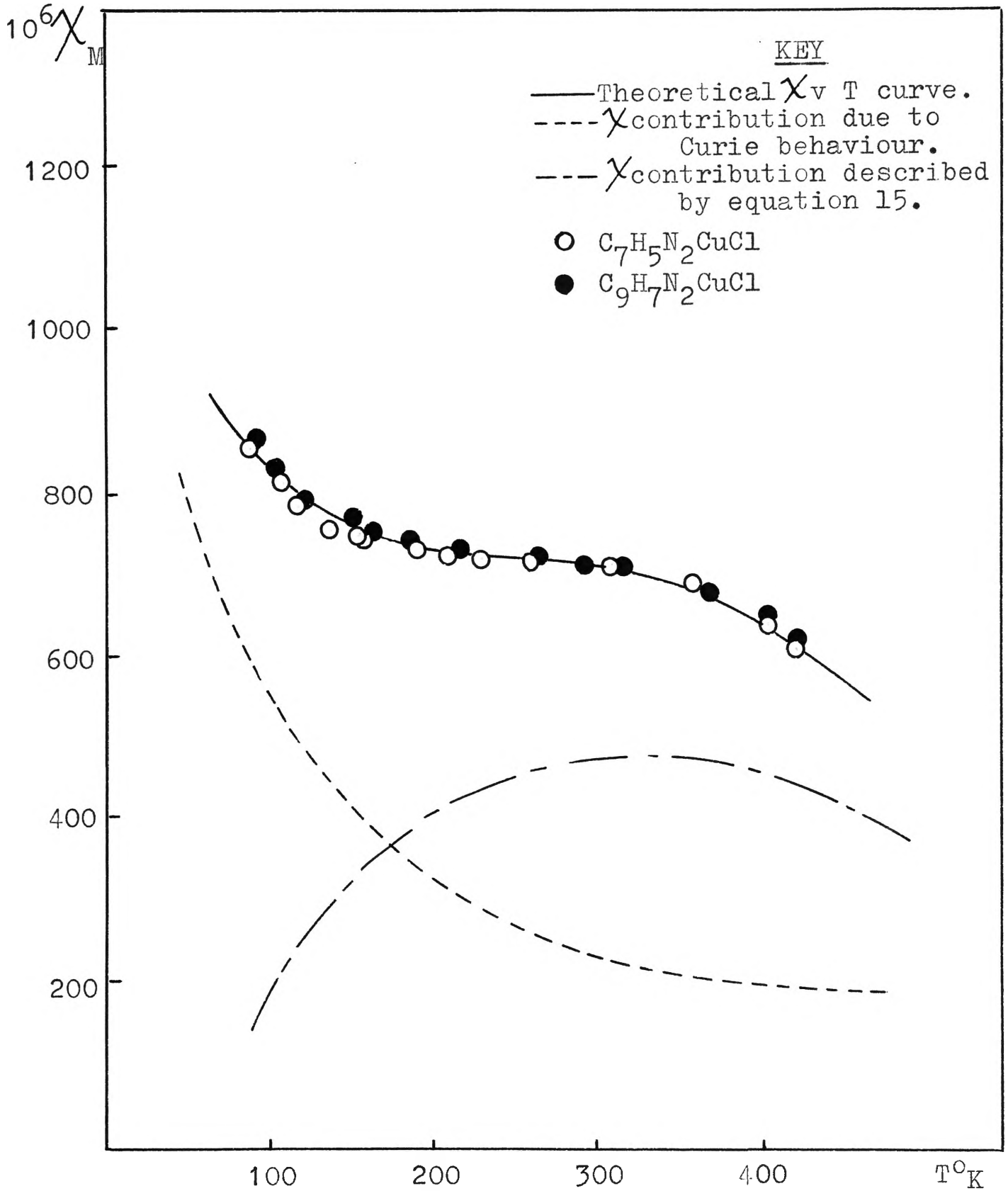


FIGURE 18 (cont.)



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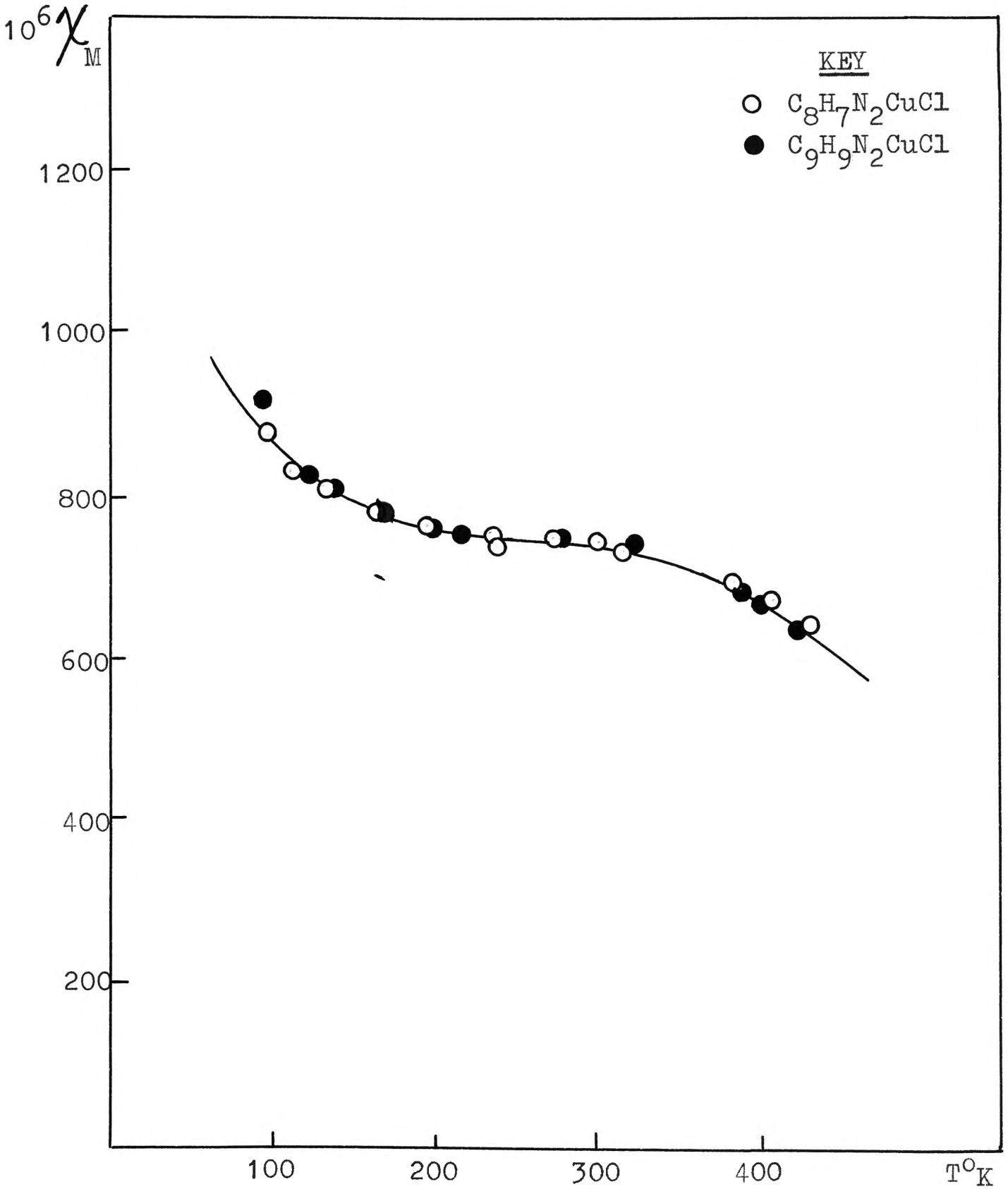

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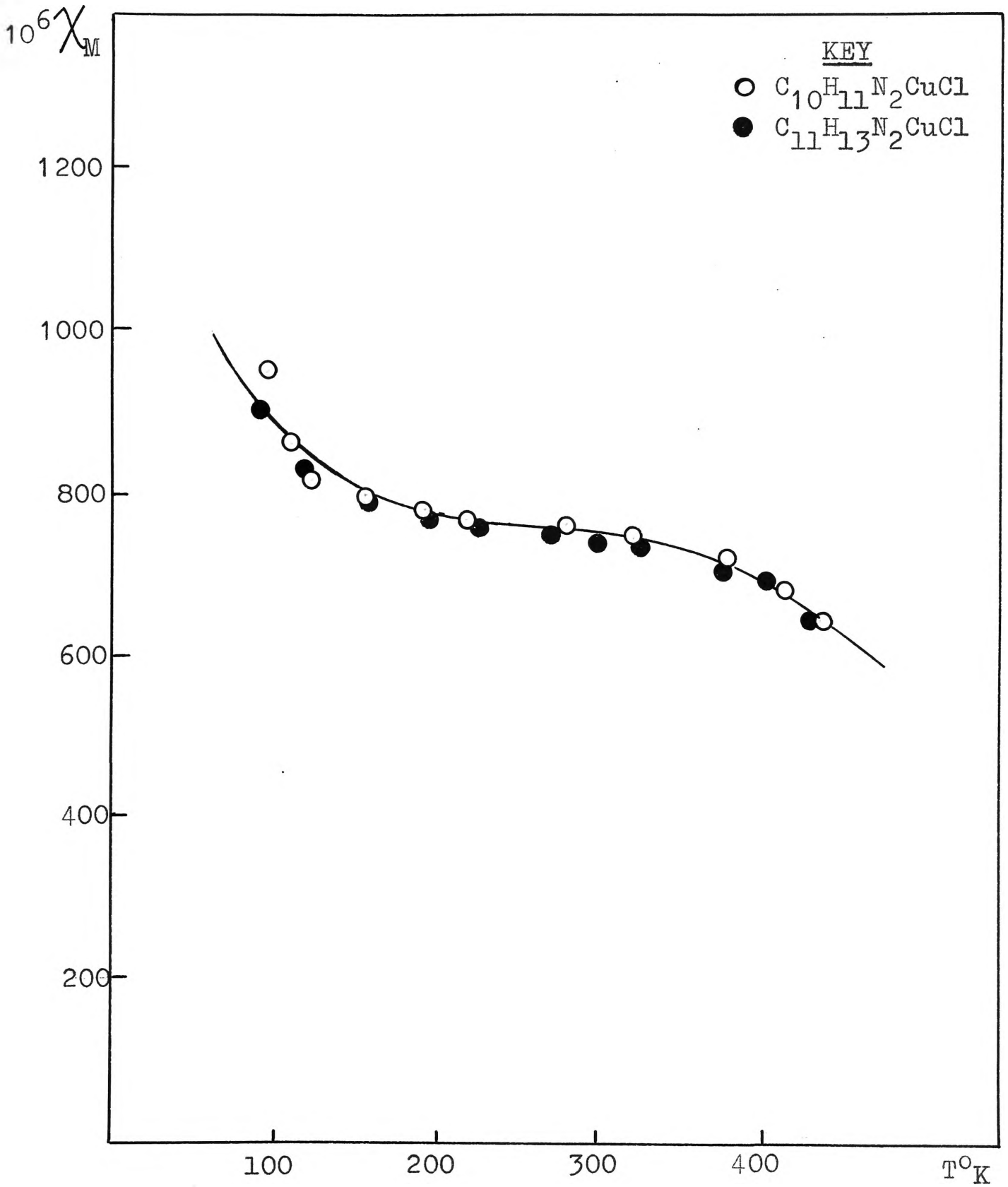

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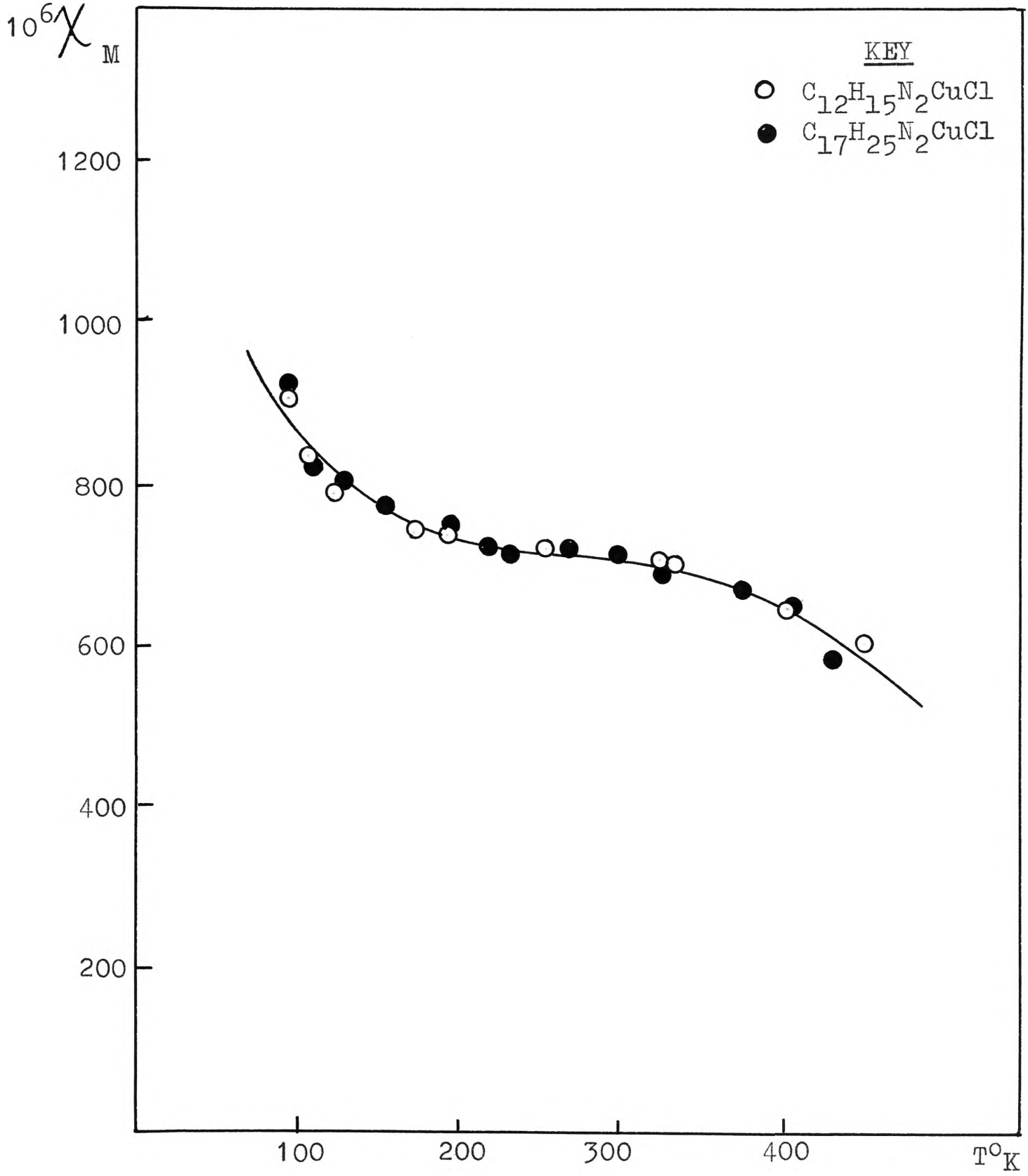

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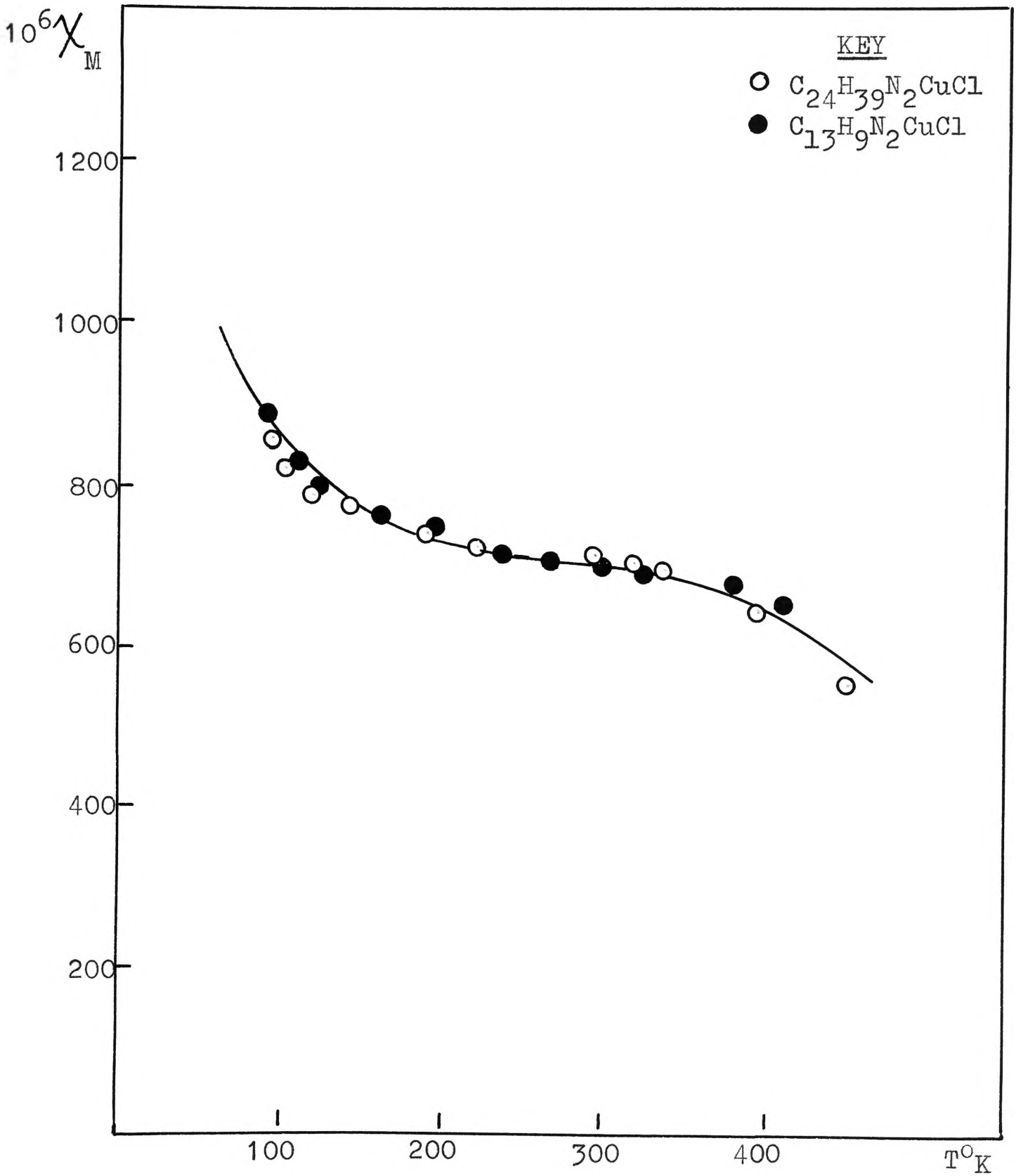

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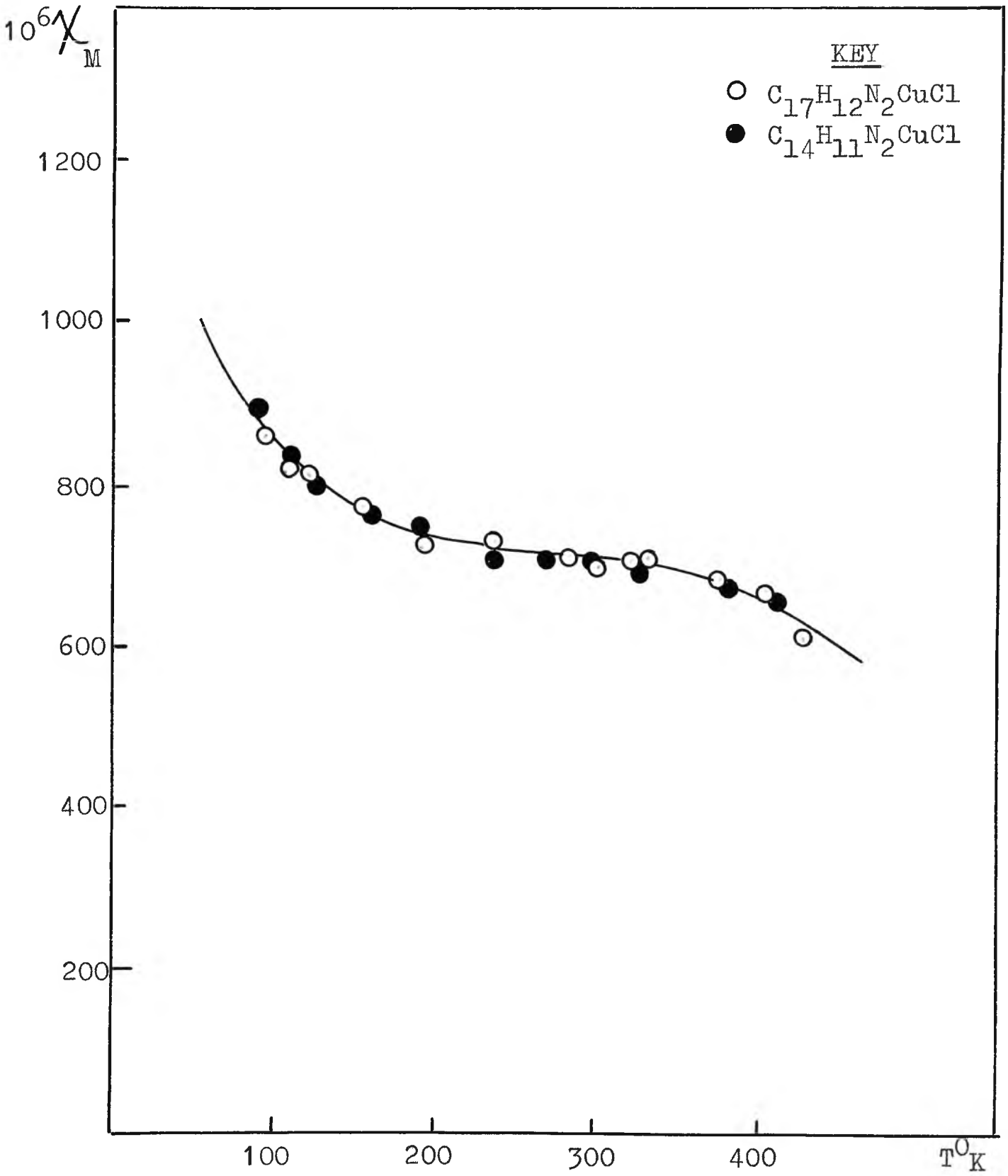

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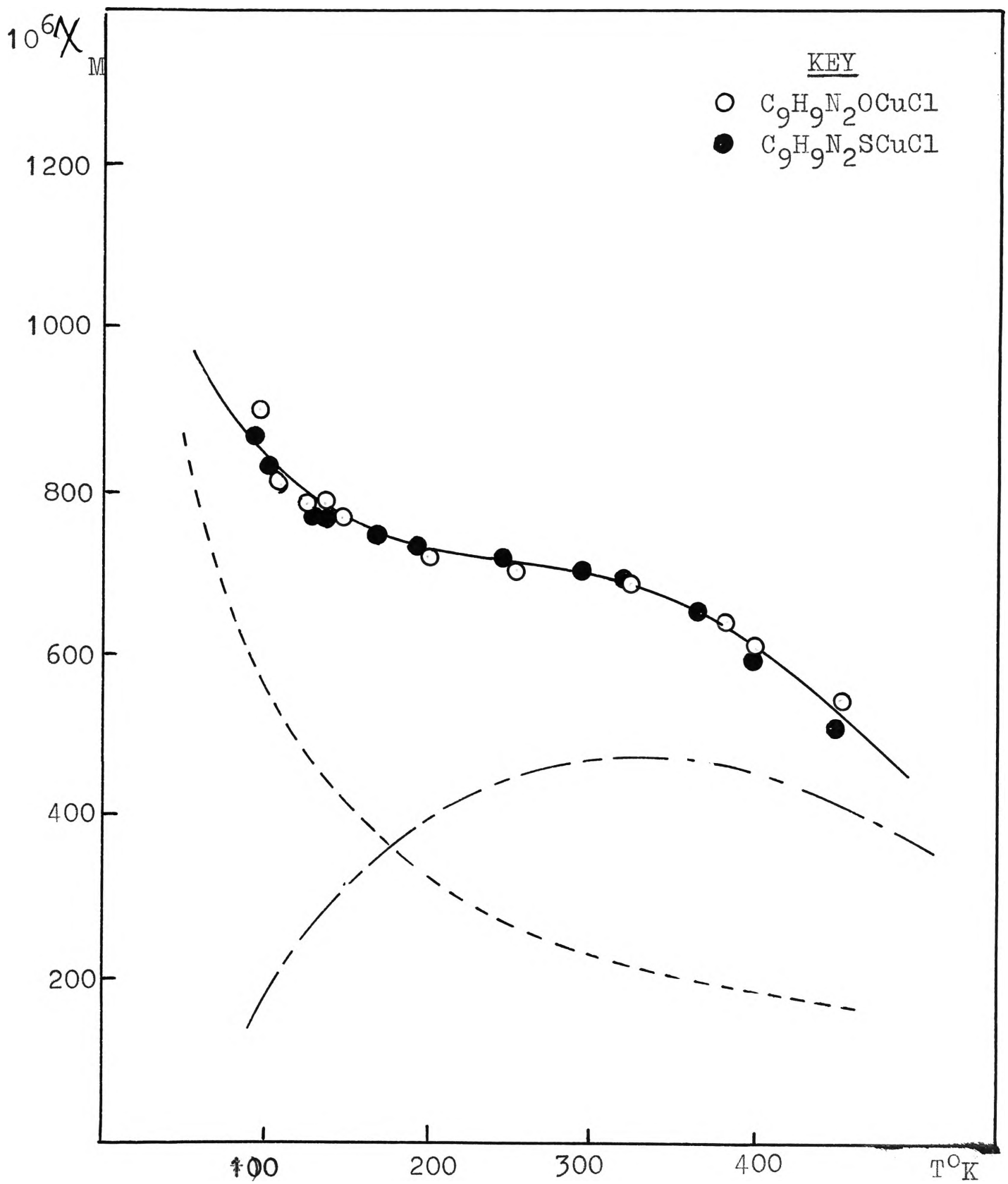

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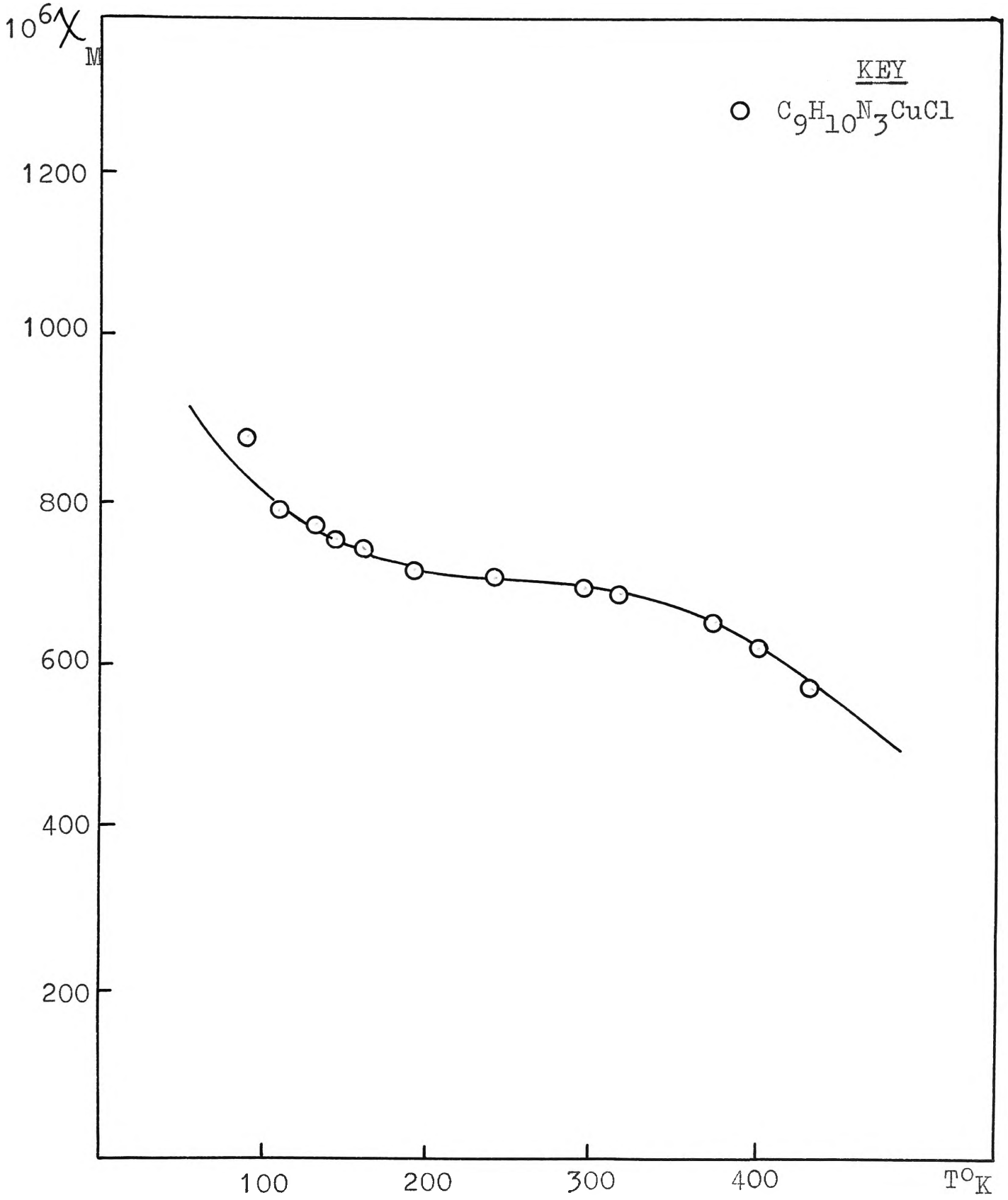

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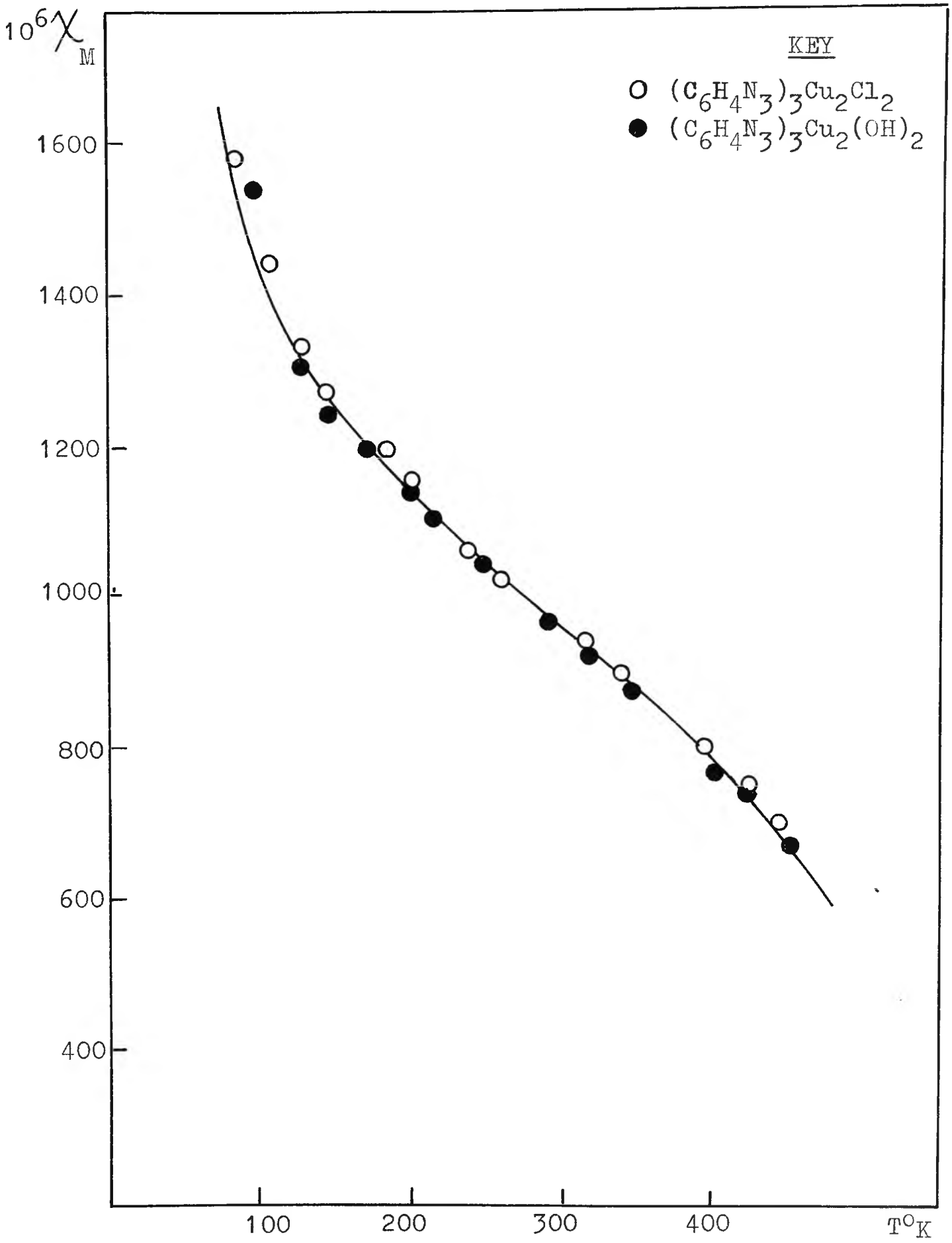
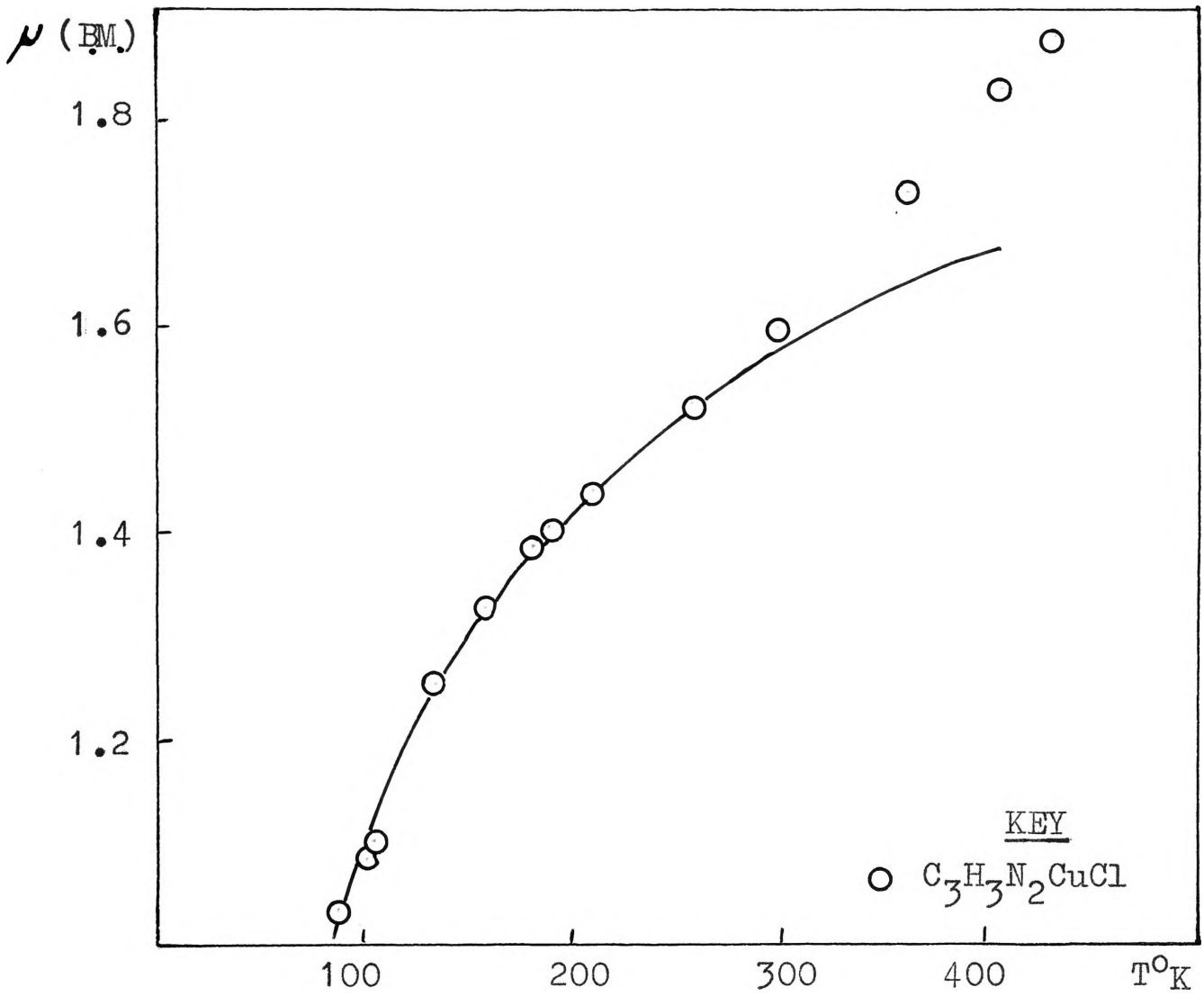


FIGURE 19.

MAGNETIC MOMENTS AT DIFFERENT TEMPERATURES OF COPPER(11) COMPLEXES OF IMIDAZOLE, BENZIMIDAZOLE, BENZOTRIAZOLE AND SUBSTITUTED BENZIMIDAZOLES.



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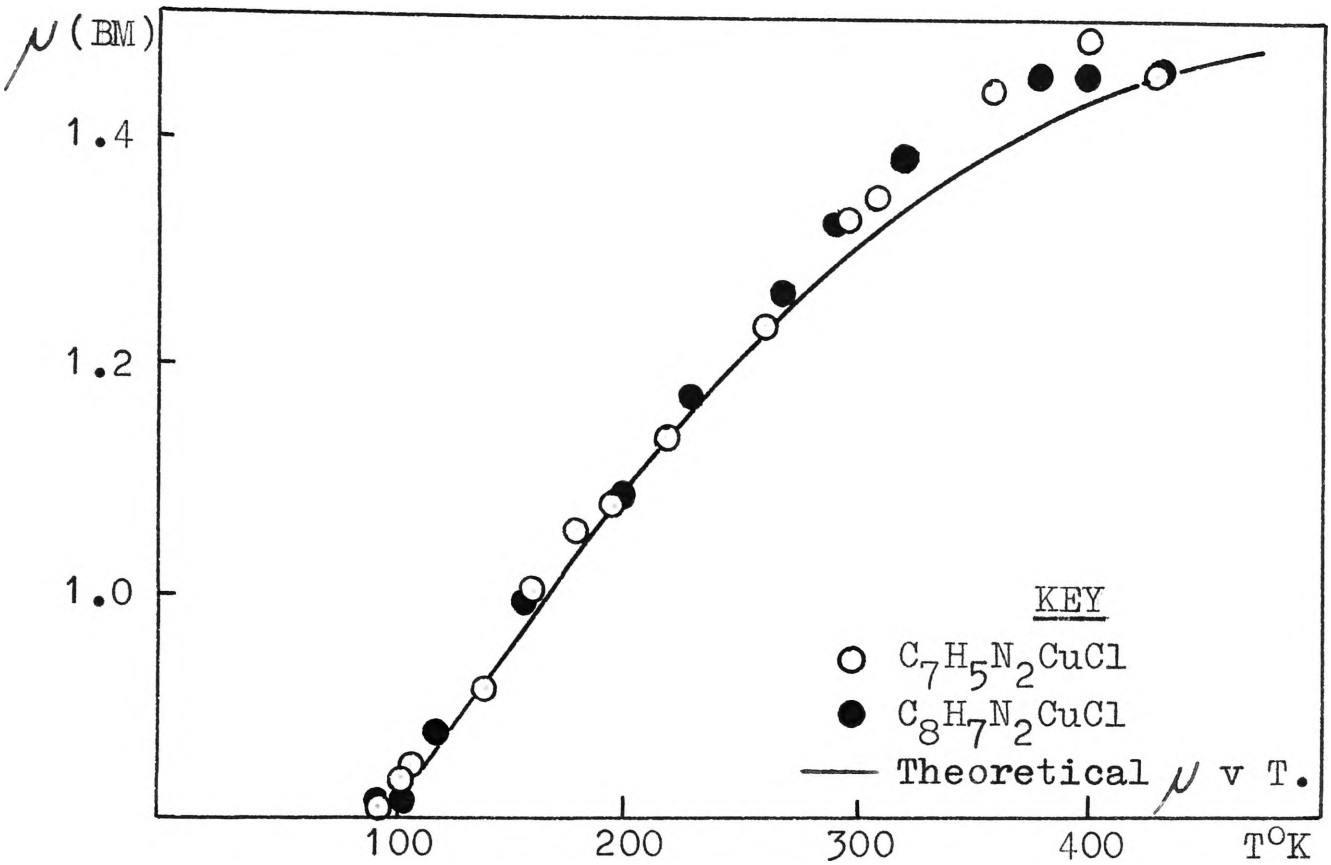

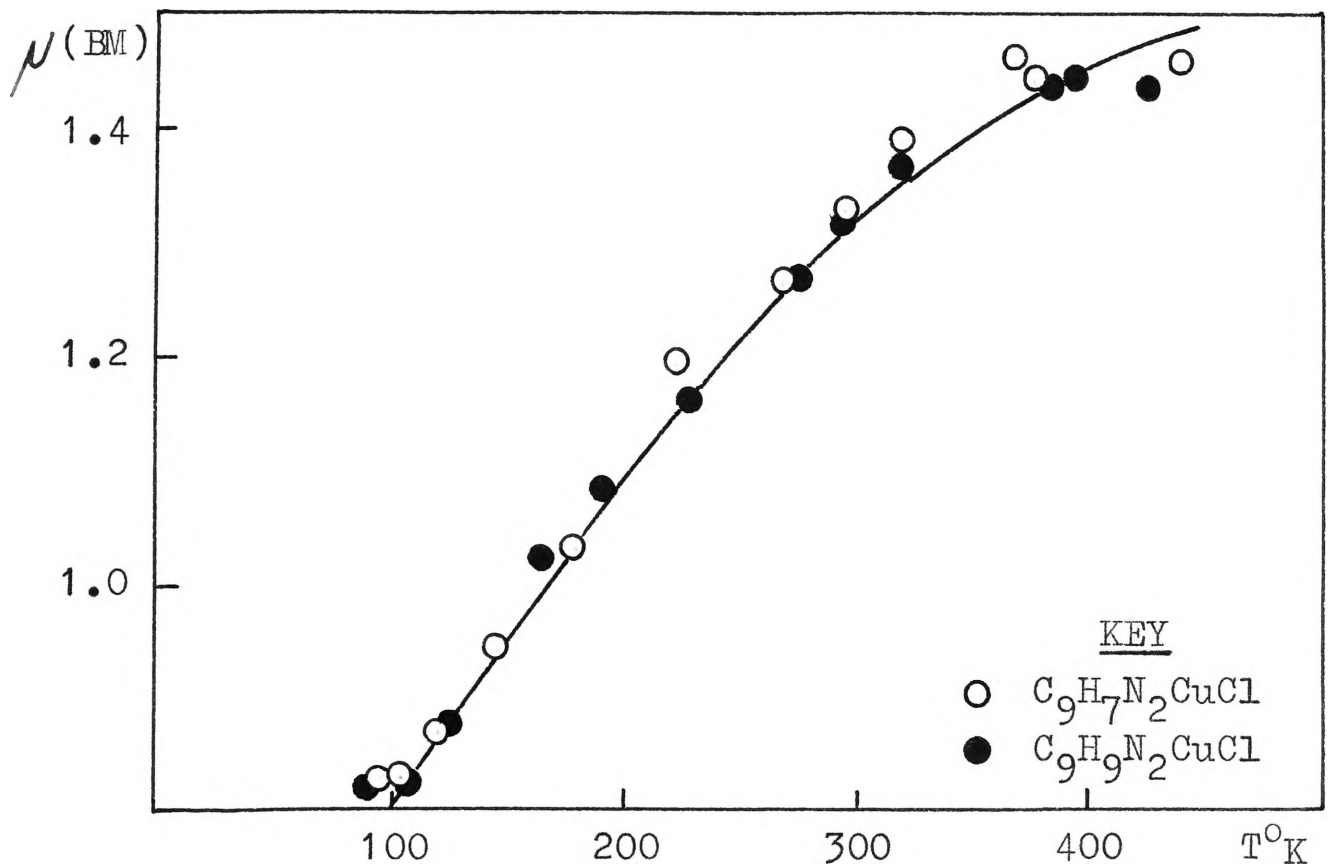

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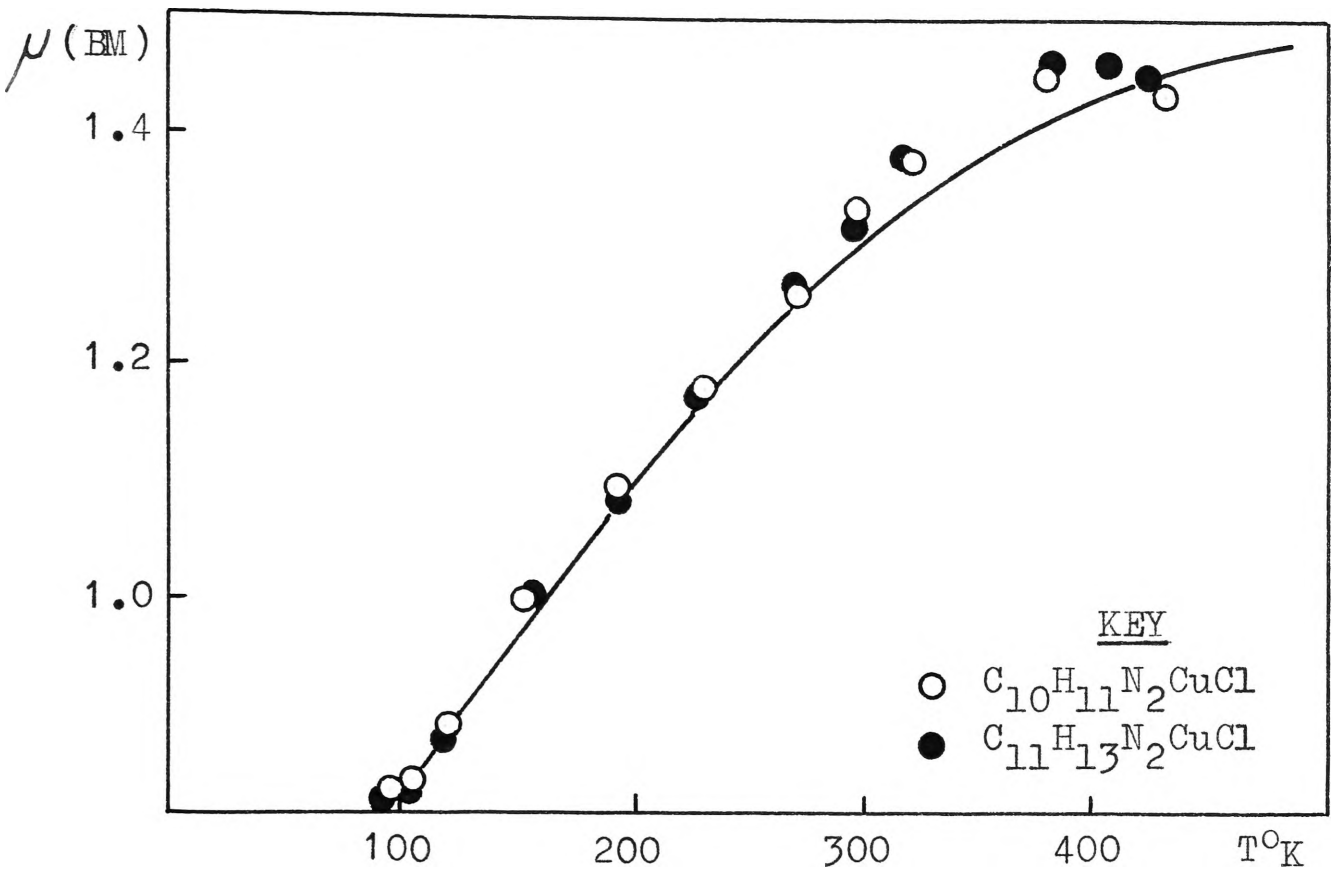


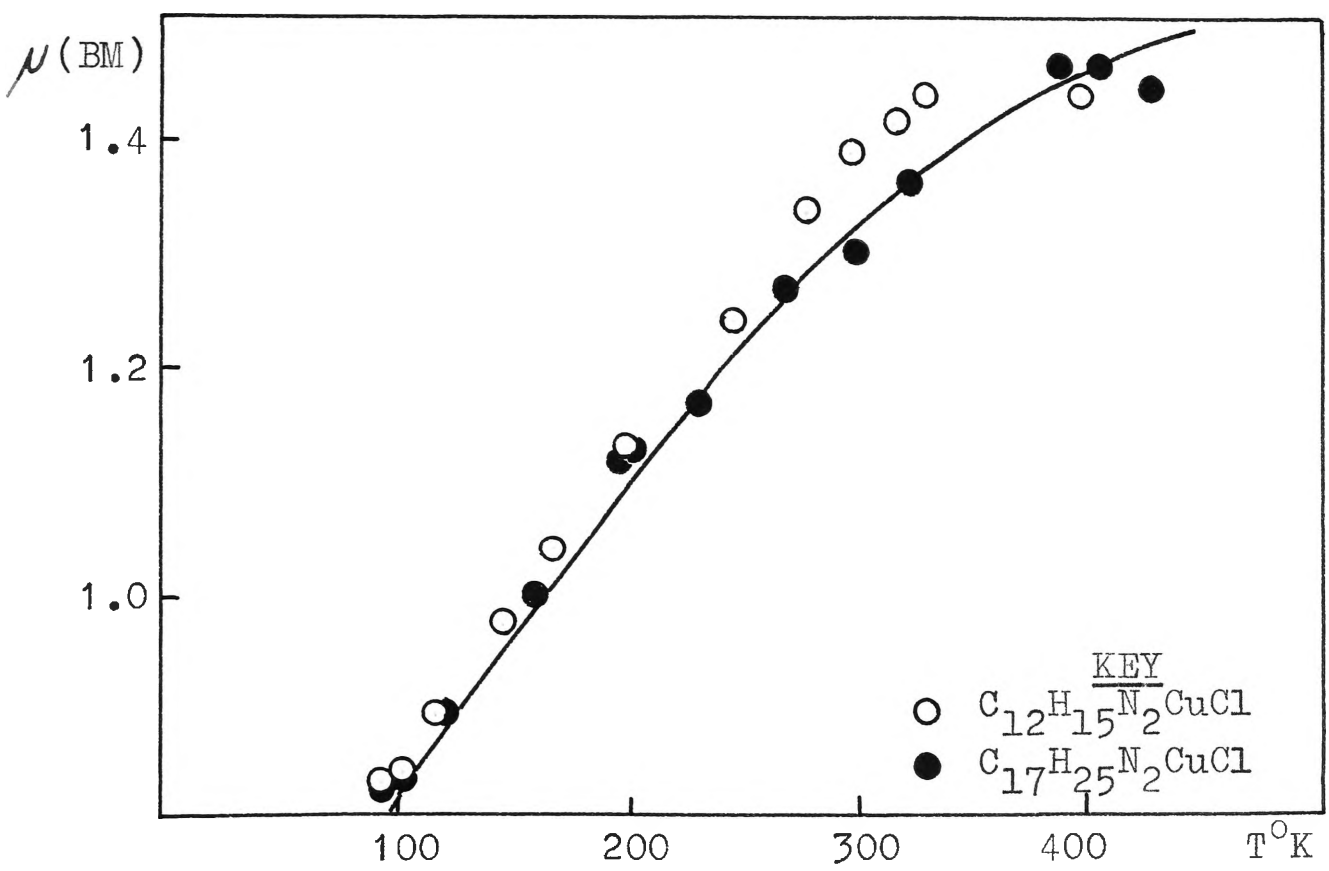


FIGURE 19 (cont.)

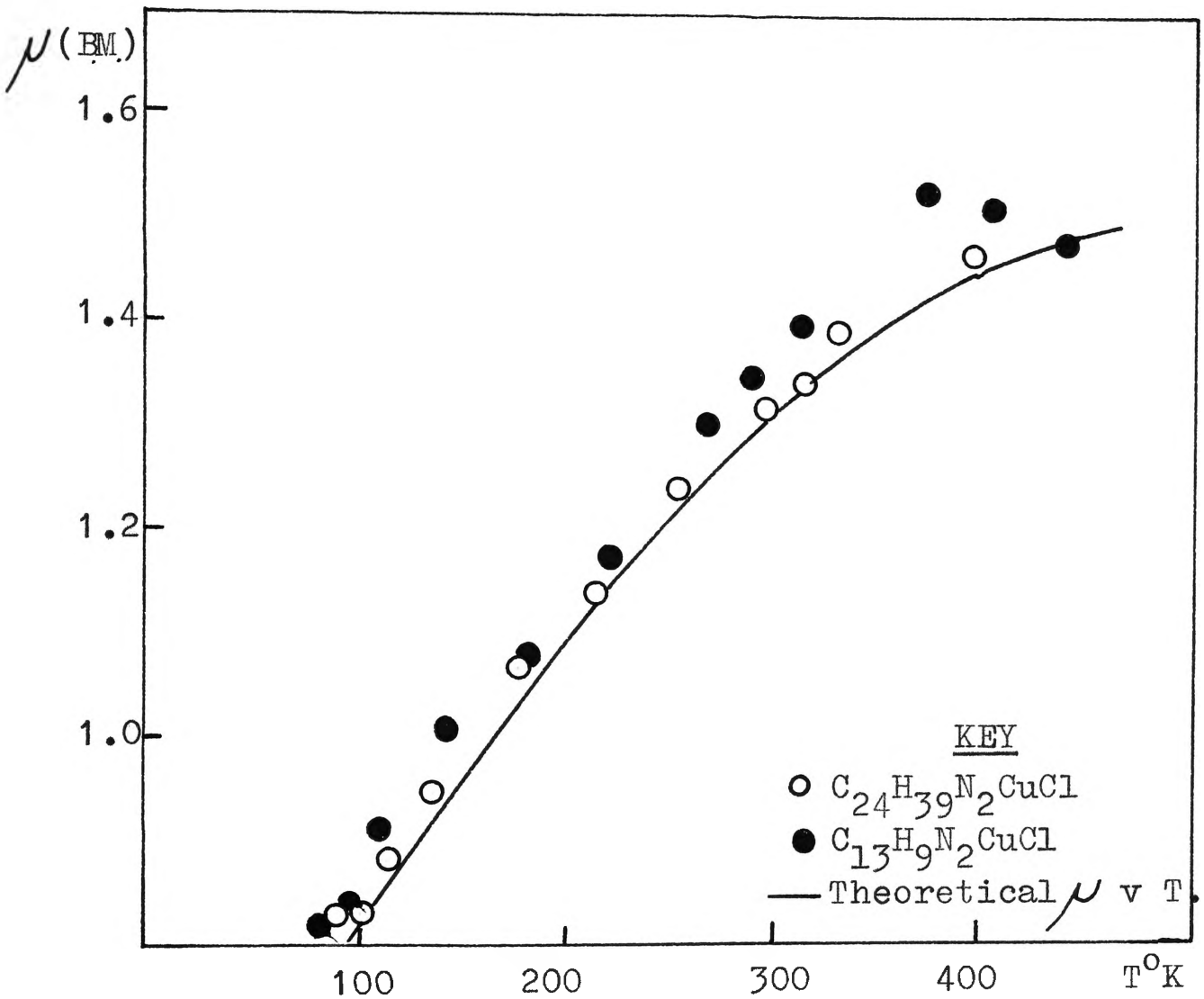


FIGURE 19 (cont.)

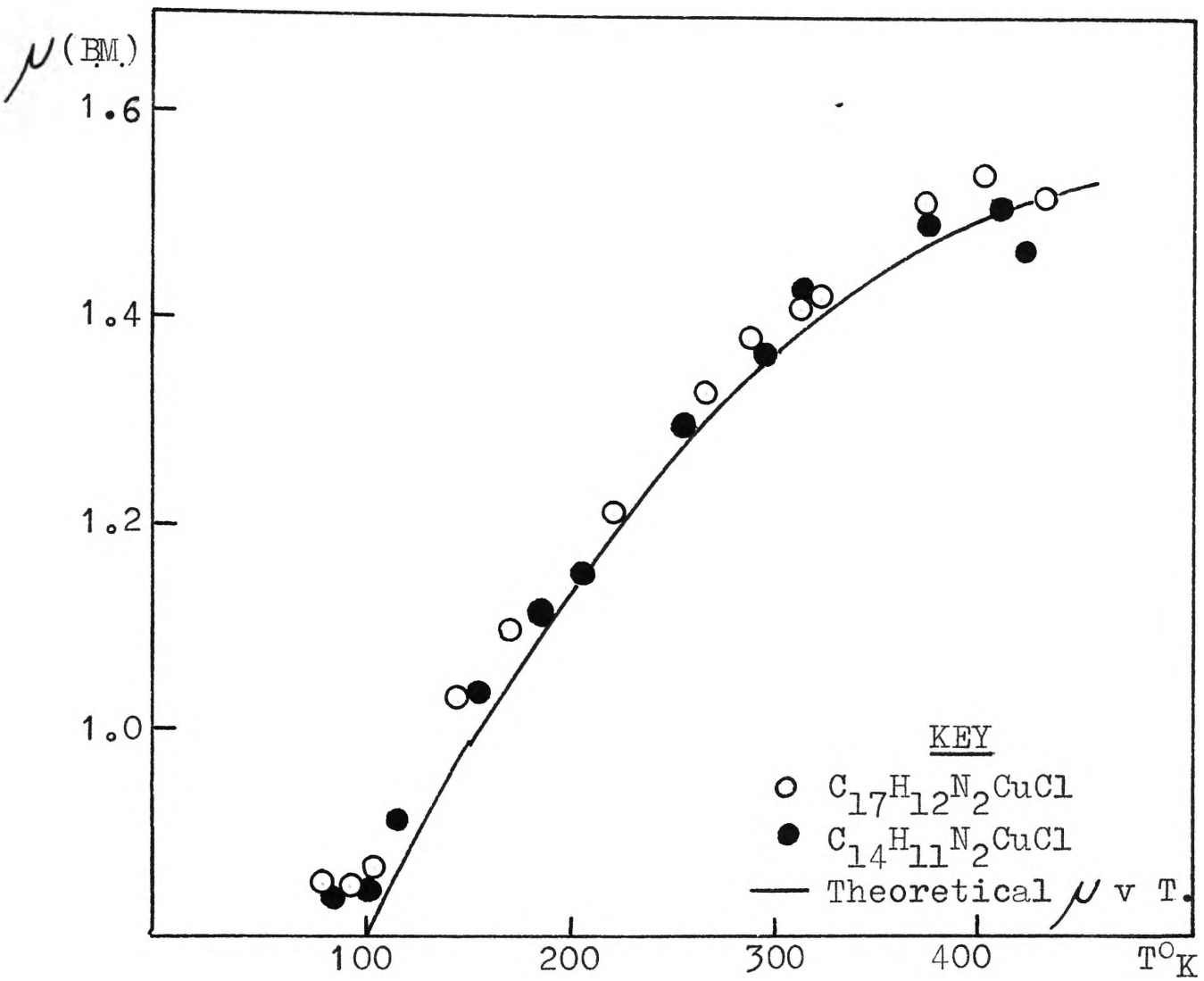
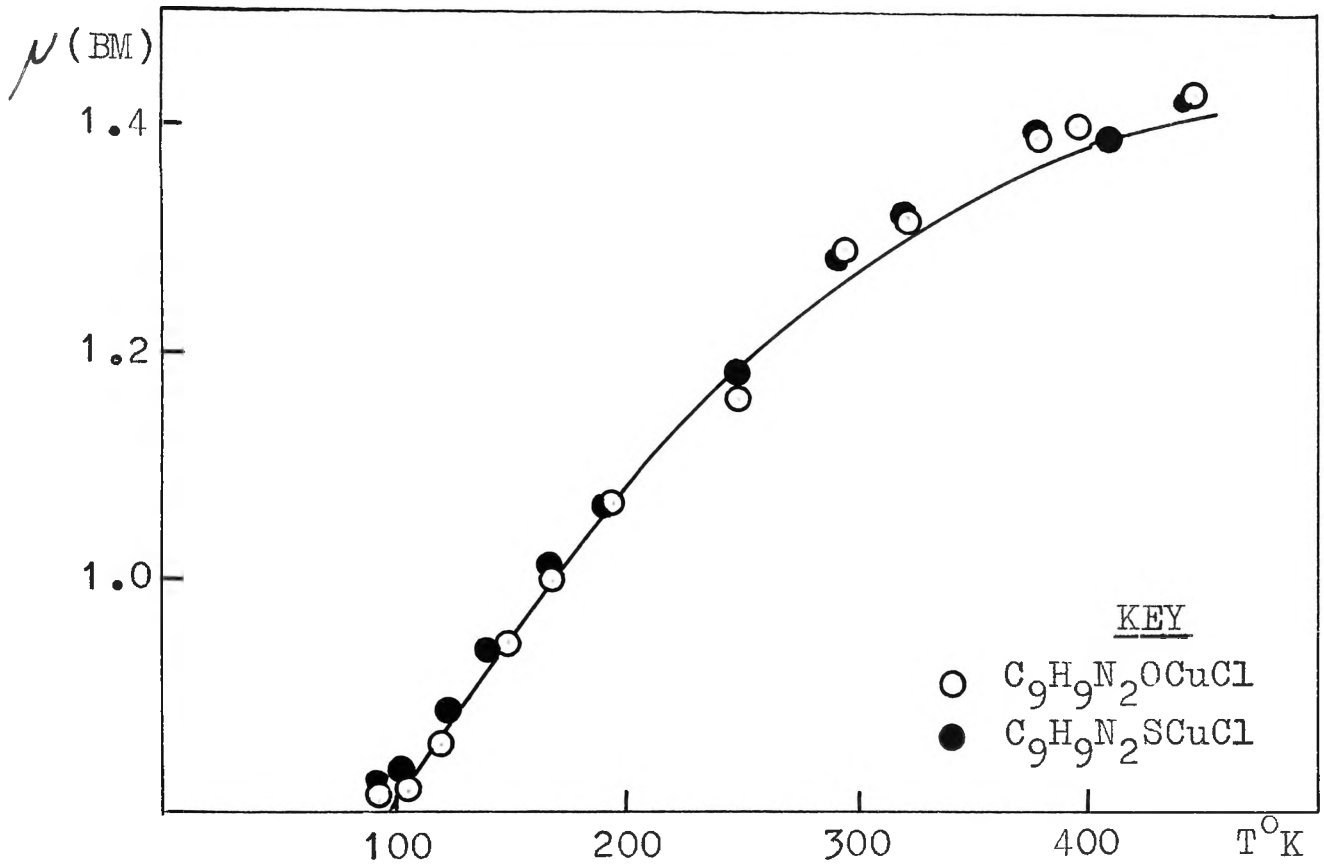


FIGURE 19 (cont.)



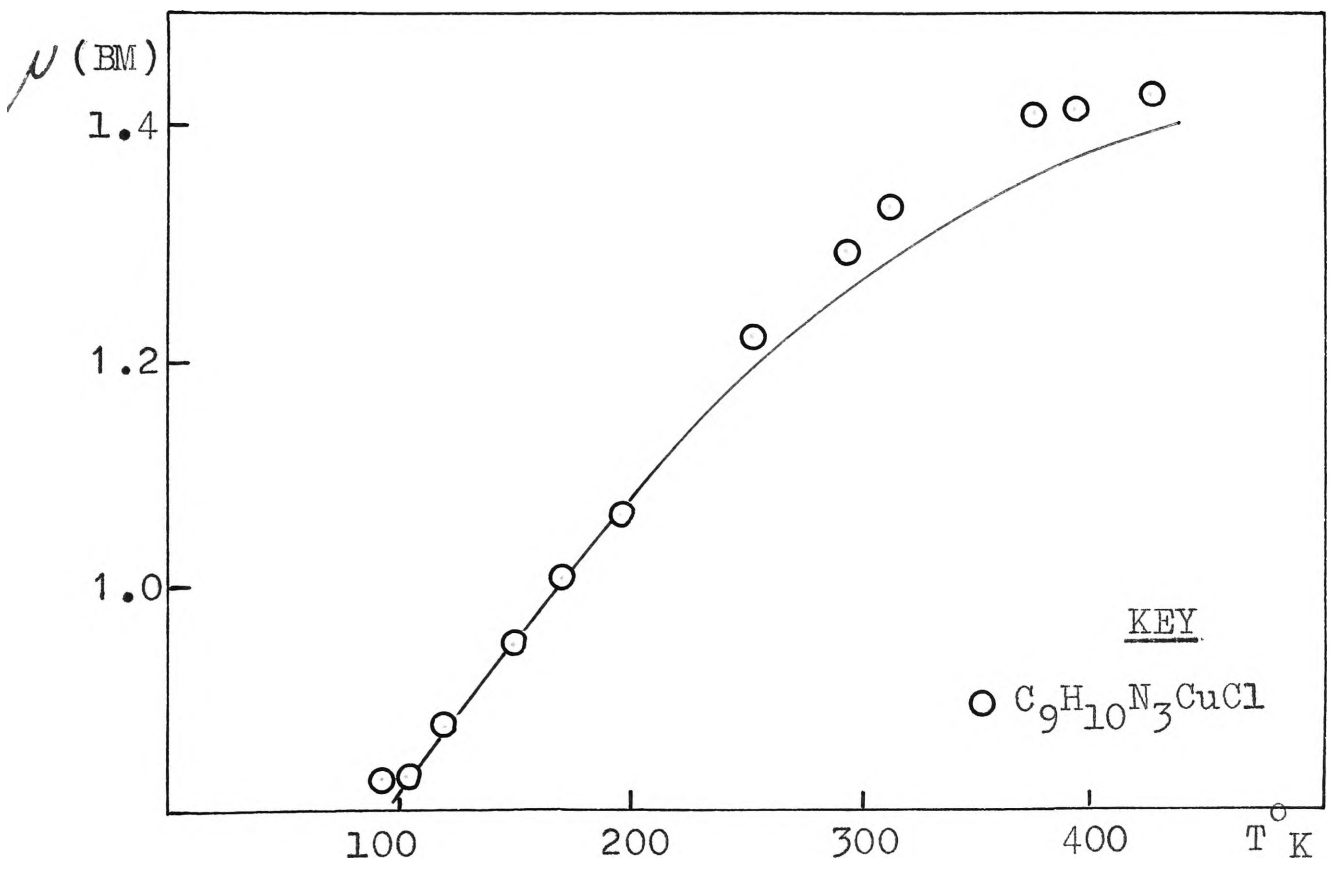


FIGURE 19 (cont.)

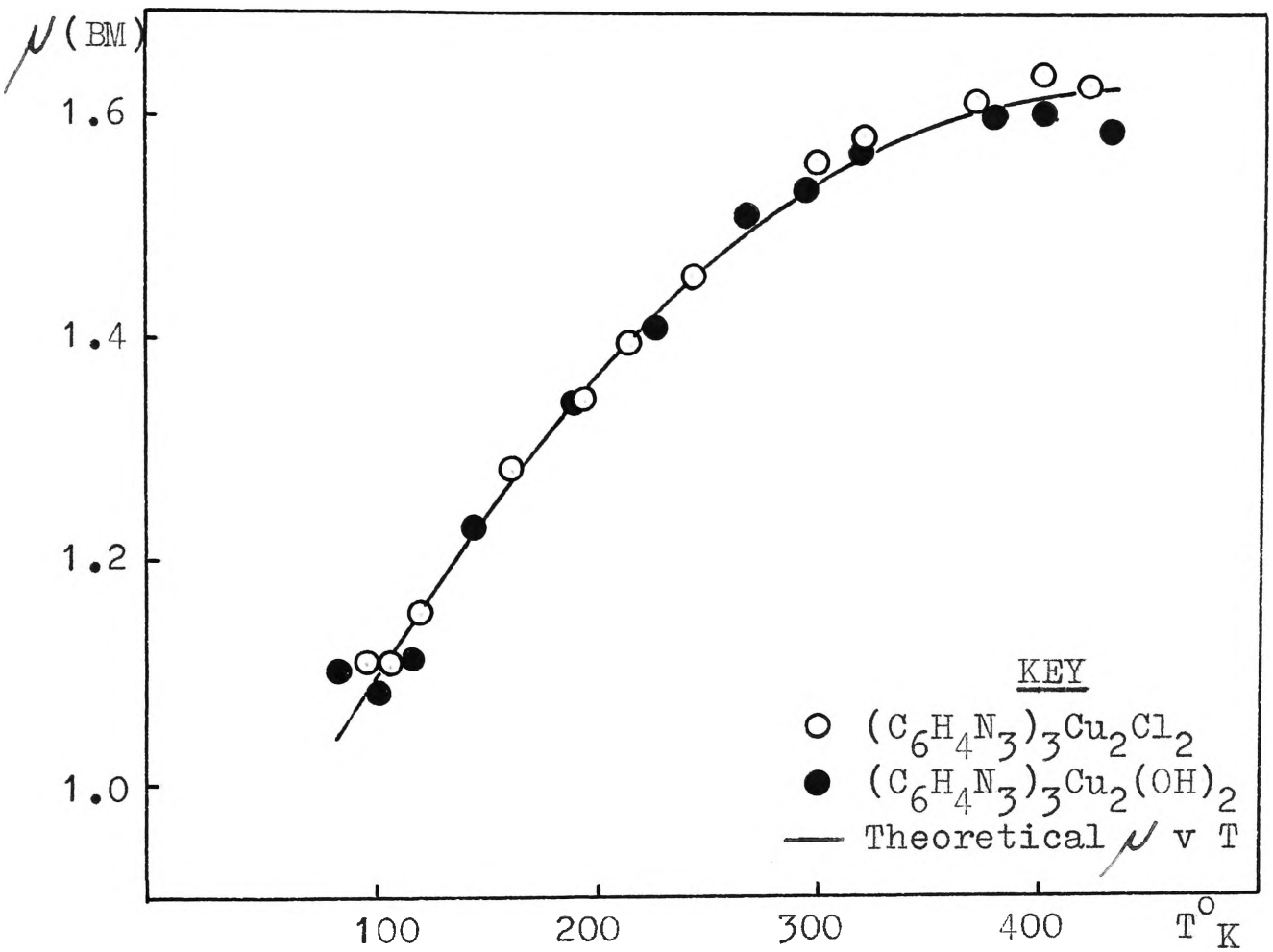


FIGURE 20 a.

STRUCTURE OF IMIDAZOLE COPPER(11) CHLORIDE.

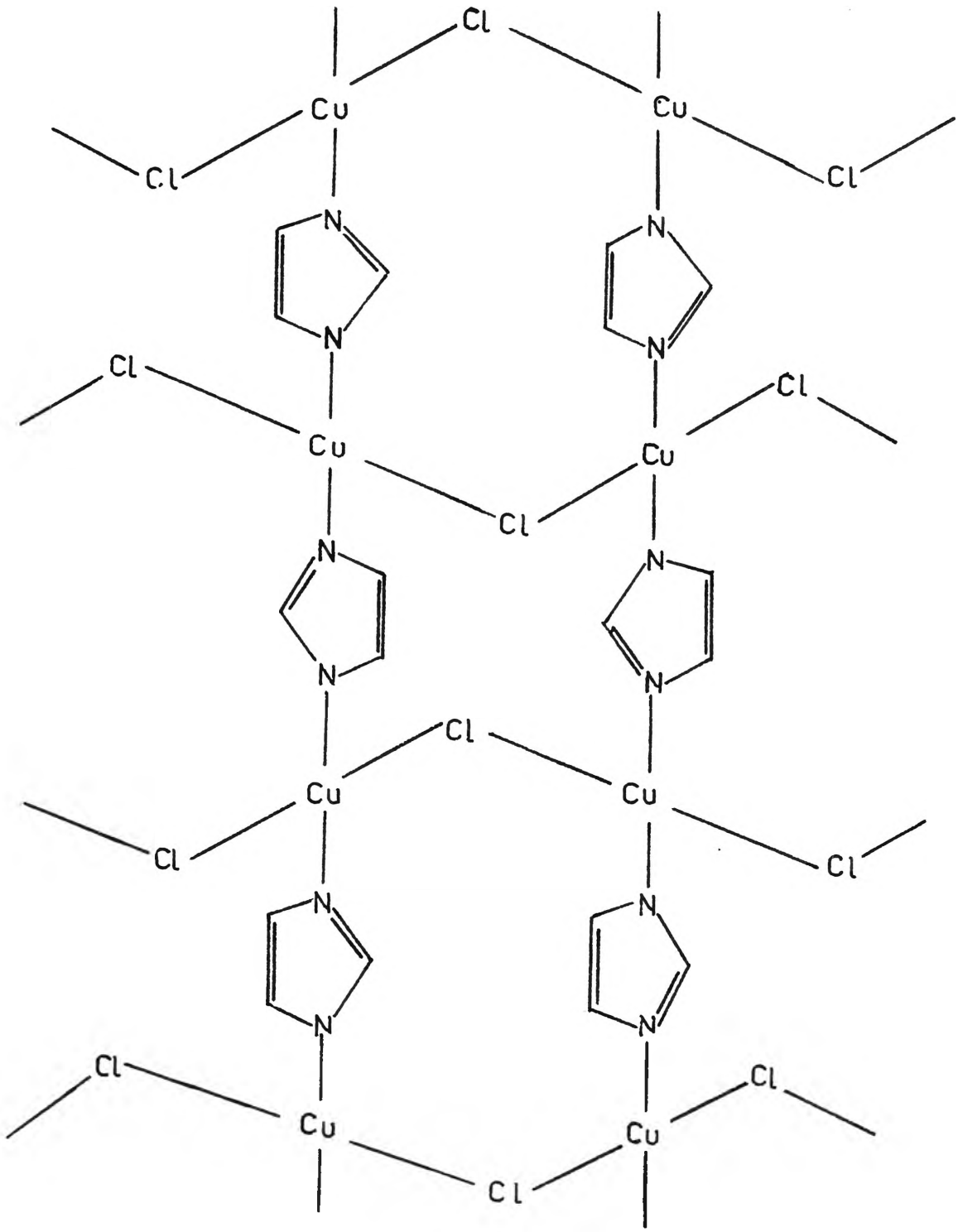
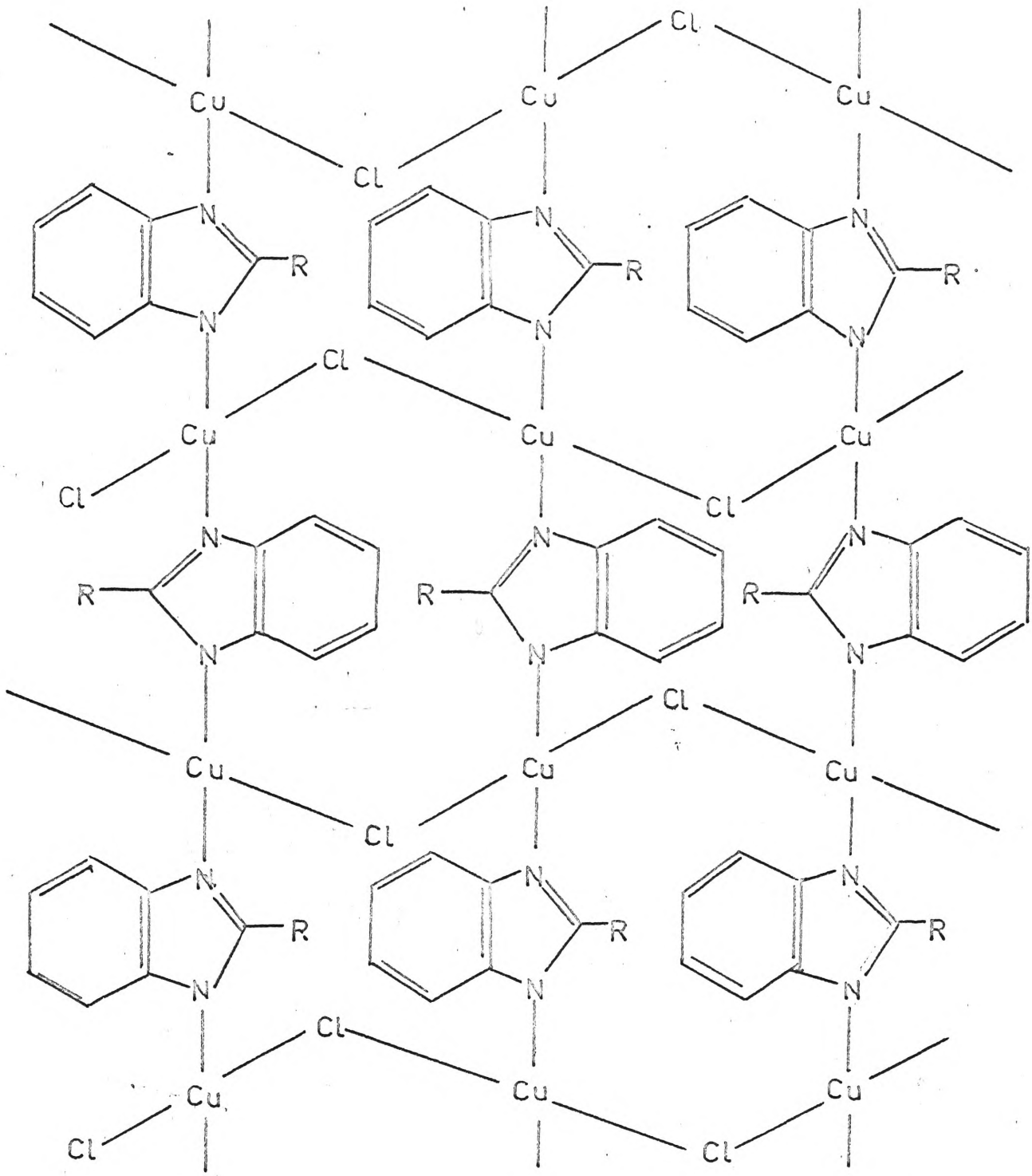


FIGURE 20 b.

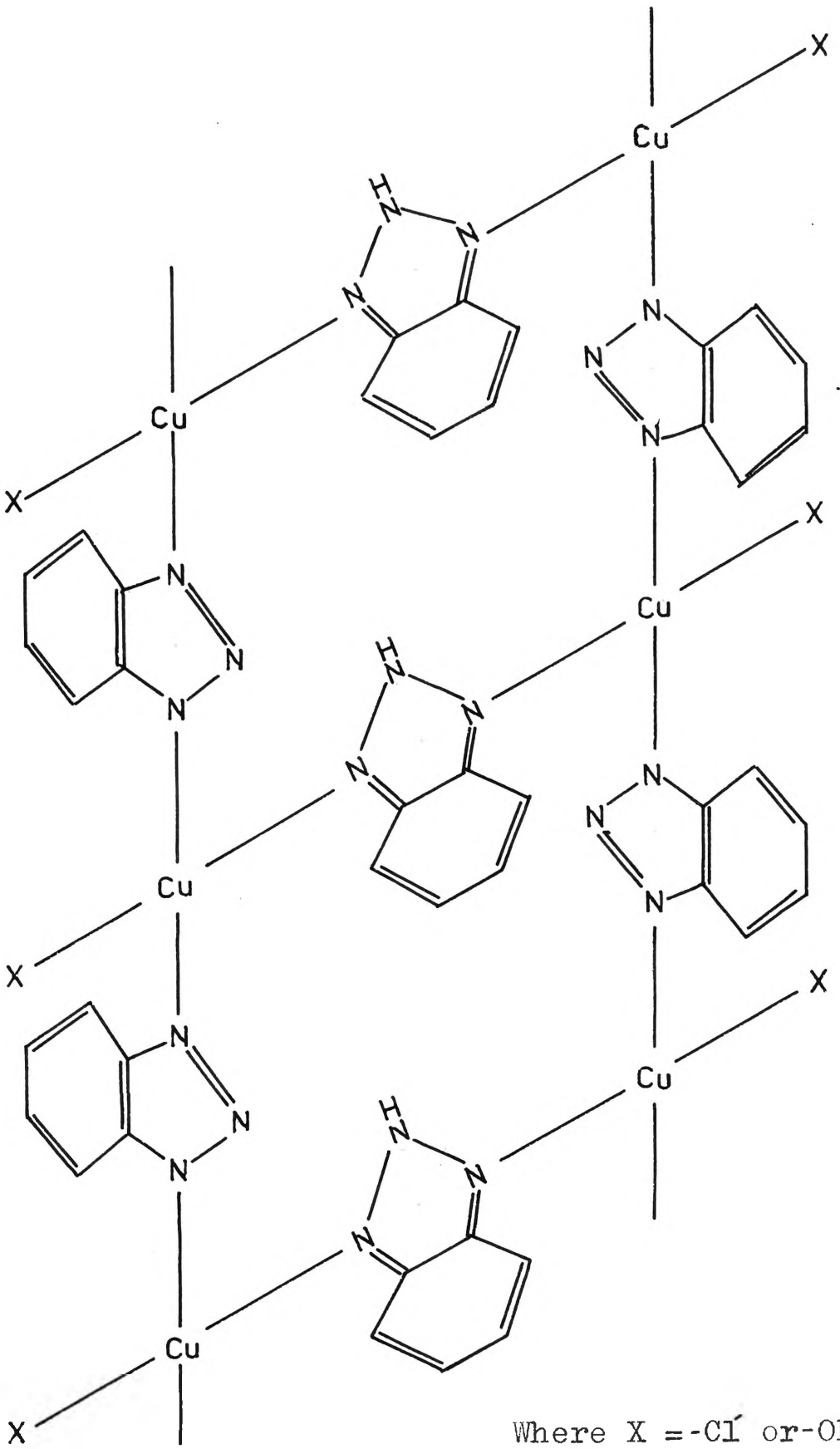
STRUCTURE OF COPPER(11) COMPLEXES OF BENZIMIDAZOLE AND SUBSTITUTED BENZIMIDAZOLES.



Where R = -H; $-CH_3$; $-C_2H_3$; $-C_2H_5$; $-C_3H_7$; $-C_4H_9$; $-C_5H_{11}$; $-C_{10}H_{21}$; $-C_{17}H_{35}$; $-C_6H_5$; $-C_{10}H_7$; $-C_7H_7$; $-CH(NH_2)CH_3$; $-CH(OH)CH_3$; $-CH(SH)CH_3$.

FIGURE 21.

STRUCTURE OF BENZOTRIAZOLE COPPER(11) COMPLEXES.



Where X =-Cl or-OH.

TABLE 11

ROOM TEMPERATURE MAGNETIC DATA FOR COPPER (II) COMPLEXES OF IMIDAZOLE, BENZIMIDAZOLE, SUBSTITUTED BENZIMIDAZOLES AND BENZOTHIAZOLE.

	COMPOUND	T°C	$10^6\chi_g$	$10^6\chi_m$	$-10^6\Delta$	$10^6\chi_m$	μ(B.M.)
1.	$(C_3H_3N_2)CuCl$	24.8	5.44	904	59.1	1063	1.60
2.	$C_7H_5N_2CuCl$	19.8	3.66	591	130.1	721	1.32
3.	$C_8H_7N_2CuCl$	18.0	2.49	588	147.9	736	1.32
4.	$C_9H_7N_2CuCl$	22.3	2.33	595	156.9	752	1.34
5.	$C_9H_9N_2CuCl$	20.4	2.32	594	165.7	759	1.31
6.	$C_{10}H_{11}N_2CuCl$	24.7	2.31	549	183.5	733	1.33
7.	$C_{11}H_{13}N_2CuCl$	21.3	2.19	537	201.3	738	1.32
8.	$C_{12}H_{15}N_2CuCl$	21.9	2.04	513	219.1	732	1.37
9.	$C_{17}H_{25}N_2CuCl$	21.5	1.89	411	308.4	719	1.28
10.	$C_{24}H_{39}N_2CuCl$	21.5	1.51	298	453.1	751	1.32
11.	$C_{13}H_9N_2CuCl$	21.7	1.21	627	143.4	770	1.35
12.	$C_{14}H_{11}N_2CuCl$	21.4	2.00	602	144.8	787	1.40
13.	$C_{17}H_{12}N_2CuCl$	21.9	1.34	513	156.7	770	1.37
14.	$C_9H_9N_2OCuCl$	21.9	2.56	573	116.0	689	1.29
15.	$C_9H_9N_2HCuCl$	22.0	2.21	503	177.0	683	1.28
16.	$C_9H_{10}N_3CuCl$	21.8	2.09	500	193.2	683	1.28
17.	$(C_6H_4N_3)_3Cu_2Cl_2$	21.4	3.77	909	109.8	1019	1.56
18.	$(C_6H_4N_3)_3Cu_2(OH)_2$	21.6	3.64	832	116.5	999	1.54

TABLE 12

EXPERIMENTAL GRAM, MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS AT DIFFERENT TEMPERATURES FOR COPPER (11) COMPLEXES OF IMIDAZOLE, BENZIMIDAZOLE AND SUBSTITUTED BENZIMIDAZOLES.

1. Imidazole Copper (11) Chloride - $(C_3H_3N_2)$ CuCl

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
96.0	7.06	1378	1.03
104.7	7.07	1381	1.08
110.1	7.04	1374	1.10
140.2	7.04	1374	1.25
160.5	6.96	1359	1.33
180.9	6.73	1315	1.39
190.7	6.50	1270	1.40
210.3	6.24	1218	1.44
260.0	5.74	1120	1.53
298.3	5.44	1063	1.60
309.9	5.39	1053	1.62
360.2	5.35	1044	1.74
403.4	5.29	1033	1.83
429.3	5.08	991	1.88

TABLE 12 (Continued)

2. Benzimidazole Copper (11) Chloride - $(C_7H_5N_2)$ CuCl

T°K	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
96.0	4.33	852	0.81
104.7	4.22	831	0.84
110.1	4.10	808	0.85
140.2	3.96	780	0.91
161.5	3.91	770	1.00
180.9	3.81	751	1.05
190.7	3.74	737	1.07
217.3	3.70	729	1.13
259.8	3.66	721	1.23
298.3	3.70	728	1.32
309.9	3.64	716	1.34
360.2	3.57	702	1.43
403.4	3.36	661	1.47
429.3	3.05	601	1.44

TABLE 12 (Continued)

3. 2-Methylbenzimidazole Copper (11) Chloride - $(C_8H_7N_2)$ CuCl

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
96.8	2.90	859	0.82
104.9	2.71	802	0.82
119.7	2.69	796	0.88
158.4	2.63	778	1.00
193.7	2.53	750	1.08
230.0	2.50	739	1.17
269.4	2.47	732	1.26
291.4	2.49	736	1.32
321.4	2.47	732	1.38
382.7	2.40	710	1.45
401.3	2.27	671	1.45
430.8	2.12	629	1.45

TABLE 12 (Continued)

4. 2-Vinylbenzimidazole Copper (11) Chloride - $(C_9H_7N_2)$ CuCl

T^oK	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
98.4	2.75	864	0.83
105.4	2.64	828	0.84
120.4	2.51	789	0.87
150.3	2.49	782	0.91
184.7	2.42	761	1.07
224.6	2.33	730	1.15
268.3	2.33	731	1.26
295.1	2.33	732	1.32
322.8	2.32	727	1.38
370.4	2.23	700	1.45
380.2	2.20	691	1.43
407.9	2.08	652	1.47
440.8	1.89	593	1.42

TABLE 12 (Continued)

5. 2-Ethylbenzimidazole Copper (11) Chloride - $(C_9H_9N_2)$ CuCl

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
97.2	2.73	858	0.83
105.9	2.58	812	0.83
122.0	2.52	793	0.88
159.8	2.81	882	1.07
192.8	2.40	754	1.08
228.0	2.35	738	1.16
274.7	2.33	732	1.27
293.4	2.32	730	1.31
316.5	2.32	729	1.36
385.7	2.08	652	1.43
396.4	2.06	647	1.44
424.7	1.97	620	1.43

TABLE 12 (Continued)

6. 2-Propylbenzimidazole Copper (11) Chloride - $(C_{10}H_{11}N_2)CuCl$

T°K	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
97.1	2.87	911	0.82
103.9	2.56	810	0.84
120.4	2.51	796	0.88
153.7	2.48	787	0.99
191.8	2.40	762	1.09
229.6	2.33	739	1.17
271.4	2.30	729	1.26
297.7	2.31	733	1.33
320.0	2.30	720	1.37
375.8	2.23	708	1.47
410.2	2.14	679	1.50
429.6	1.93	612	1.43

TABLE 12 (Continued)

7. 2-Butylbenzimidazole Copper (11) Chloride - $(C_{11}H_{13}N_2)CuCl$

$T^{o}K$	$10^{6}\chi_g$	$10^{6}\chi_m$	μ (B.M.)
95.4	2.58	872	0.82
102.6	2.41	812	0.82
117.8	2.37	800	0.87
162.3	2.34	788	1.02
190.8	2.26	761	1.08
227.4	2.22	750	1.17
268.1	2.21	746	1.27
294.3	2.19	738	1.32
321.6	2.16	730	1.38
383.7	2.09	706	1.45
403.4	1.93	651	1.46
426.8	1.78	602	1.44

TABLE 12 (Continued)

8. 2-Pentylbenzimidazole Copper (11) Chloride - $(C_{12}H_{15}N_2)CuCl$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
97.4	2.39	858	0.82
104.2	2.29	821	0.83
119.8	2.20	789	0.88
145.0	2.18	782	0.96
168.6	2.18	780	1.03
196.8	2.09	749	1.09
250.4	2.06	737	1.22
281.1	2.04	732	1.32
294.9	2.04	731	1.37
320.4	2.03	728	1.39
329.4	1.84	659	1.42
400.9	1.70	608	1.40
447.6	1.31	471	1.30

TABLE 12 (Continued)

9. 2-Decylbenzimidazole Copper (11) Chloride - $(C_{17}H_{25}N_2)CuCl$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
96.9	2.27	863	0.80
103.4	2.13	812	0.82
121.6	2.10	800	0.89
154.1	2.08	791	0.99
197.4	2.00	761	1.10
206.3	1.92	733	1.10
227.8	1.92	730	1.16
266.7	1.92	731	1.26
294.5	1.89	719	1.28
320.8	1.86	708	1.35
380.0	1.81	689	1.45
401.7	1.70	649	1.45
424.9	1.53	583	1.41

TABLE 12 (Continued)

10. 2-Stearylbenzimidazole Copper (11) Chloride - $(C_{24}H_{39}N_2)CuCl$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
97.8	1.78	862	0.82
102.8	1.69	818	0.82
117.4	1.62	787	0.86
140.0	1.61	779	0.94
180.3	1.59	768	1.06
214.0	1.54	747	1.14
258.5	1.52	738	1.24
294.5	1.51	734	1.32
315.9	1.51	731	1.34
330.3	1.49	722	1.39
396.1	1.39	671	1.47
449.5	1.16	560	1.43

TABLE 12 (Continued)

11. 2-Phenylbenzimidazole Copper (II) Chloride - $(C_{13}H_9N_2)CuCl$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
94.8	1.39	878	0.82
101.3	1.35	851	0.83
120.6	1.34	842	0.91
151.2	1.32	832	1.01
190.4	1.23	776	1.09
227.1	1.23	776	1.18
274.4	1.22	771	1.31
293.7	1.22	770	1.35
318.8	1.22	768	1.40
382.4	1.21	762	1.54
400.6	1.13	711	1.52
422.9	1.03	649	1.49

TABLE 12 (Continued)

12. 2-Benzylbenzimidazole Copper (11) Chloride - $(C_{17}H_{12}N_2)CuCl$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
97.4	2.27	889	0.84
105.6	2.14	837	0.84
120.2	2.13	834	0.85
155.5	2.13	831	1.02
180.7	2.05	800	1.08
227.9	2.04	797	1.19
272.4	2.04	797	1.32
294.9	2.00	783	1.37
319.7	1.97	770	1.40
327.4	1.92	751	1.41
380.4	1.90	742	1.51
407.7	1.84	721	1.54
418.8	1.66	651	1.48

TABLE 12 (Continued)

13. 2-Naphthylbenzimidazole Copper (11) Chloride - $(C_{14}H_{11}N_2)CuCl$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
98.4	1.52	892	0.84
107.8	1.43	839	0.86
120.6	1.44	843	0.91
160.3	1.42	830	1.04
190.7	1.39	813	1.12
233.4	1.37	801	1.23
265.4	1.36	794	1.30
294.4	1.34	787	1.37
320.7	1.32	776	1.42
380.7	1.23	720	1.49
406.3	1.11	651	1.46

TABLE 12 (Continued)

14. 2-α-Hydroxyethylbenzimidazole Copper (11) Chloride - $C_9H_9N_2O$ CuCl

T^oK	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
97.2	3.13	842	0.81
104.6	2.93	789	0.82
119.4	2.82	757	0.86
147.0	2.83	761	0.95
168.3	2.75	740	1.00
197.5	2.67	718	1.07
252.3	2.61	701	1.17
297.4	2.56	689	1.29
320.1	2.50	671	1.32
380.7	2.34	628	1.39
400.0	2.23	600	1.39
450.3	2.05	552	1.42

TABLE 12 (Continued)

15. 2-α-Mercaptoethylbenzimidazole Copper (11) Chloride - $C_9H_9N_2S$ CuCl

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
97.1	2.78	862	0.82
104.6	2.66	813	0.83
123.6	2.49	771	0.88
140.9	2.46	762	0.93
172.2	2.39	739	1.01
195.4	2.32	717	1.06
250.8	2.72	702	1.19
294.8	2.21	683	1.28
320.8	2.17	671	1.32
381.7	2.01	623	1.38
402.6	1.91	591	1.38
444.6	1.78	550	1.41

TABLE 12 (Continued)

16. 2-α-Aminoethylbenzimidazole Copper (11) Chloride - $C_9H_{10}N_3$ CuCl

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
95.8	2.71	887	0.83
103.7	2.43	795	0.82
121.6	2.36	772	0.87
144.9	2.32	759	0.94
169.3	2.24	732	1.00
195.8	2.18	714	1.06
257.4	2.14	701	1.21
295.0	2.09	683	1.28
315.9	2.07	677	1.32
380.4	1.95	639	1.40
397.6	1.87	610	1.40
428.4	1.77	579	1.41

TABLE 12 (Continued)

17. Benzotriazole Copper (11) Chloride - $(C_6H_4N_3)_3\ Cu_2Cl_2$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
98.4	5.64	1526	1.10
105.6	5.22	1413	1.10
120.4	5.00	1352	1.15
159.4	4.73	1281	1.28
180.7	4.55	1230	1.34
213.5	4.17	1128	1.39
240.3	4.08	1104	1.46
294.4	3.77	1019	1.56
315.8	3.63	983	1.58
370.4	3.24	876	1.62
400.3	3.06	829	1.64
420.8	2.88	780	1.63

TABLE 12 (Continued)

18. Benzotriazole Copper (11) Hydroxide - $(C_6H_4N_3)_3Cu_2(OH)_2$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
96.7	5.87	1608	1.12
106.4	5.03	1380	1.09
120.4	4.81	1319	1.12
147.6	4.67	1280	1.24
190.9	4.31	1182	1.35
224.3	4.04	1108	1.42
272.6	3.83	1050	1.52
294.4	3.64	999	1.54
318.8	3.53	968	1.58
380.4	3.07	842	1.61
398.7	2.92	803	1.61
429.6	2.71	744	1.60

TABLE 13

PHYSICAL PROPERTIES OF COPPER (11) COMPLEXES OF IMIDAZOLE, BENZIMIDAZOLE, BENZOTRIAZOLE AND SUBSTITUTED BENZIMIDAZOLE

	COMPOUND	COLOUR	BEHAVIOUR ON HEATING	SOLUBILITY						
				Water	Acetone	Isopropyl Alcohol	Chloroform	Ether	Ammonia S.G. 0.91	0.1N HCl
1.	$C_3H_cN_2CuCl$	Brown	Decomposes above 285°C Darkens to a Black Residue	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Colourless Solution
2.	$C_7H_5N_2CuCl$	Brick Red	" "	"	"	"	"	"	"	"
3.	$C_8H_7N_2CuCl$	Reddish Brown	" "	"	"	"	"	"	"	"
4.	$C_9H_7N_2CuCl$	"	" "	"	"	"	"	"	"	"
5.	$C_9H_9N_2CuCl$	"	" "	"	"	"	"	"	"	"
6.	$C_{10}H_{11}N_2CuCl$	"	" "	"	"	"	"	"	"	"
7.	$C_{11}H_{13}N_2CuCl$	"	" "	"	"	"	"	"	"	"
8.	$C_{12}H_{15}N_2CuCl$	"	" "	"	"	"	"	"	"	"
9.	$C_{17}H_{25}N_2CuCl$	"	" "	"	"	"	"	"	"	"
10.	$C_{24}H_{39}N_2CuCl$	"	" "	"	"	"	"	"	"	"
11.	$C_{13}H_9N_2CuCl$	Chocolate Brown	" "	"	"	"	"	"	"	"
12.	$C_{14}H_{11}N_2CuCl$	"	" "	"	"	"	"	"	"	"
13.	$C_{17}H_{12}N_2CuCl$	"	" "	"	"	"	"	"	"	"
14.	$C_9H_9N_2OCuCl$	Yellowish	" "	"	"	"	"	"	"	"
15.	$C_9H_9N_2SCuCl$	"	" "	"	"	"	"	"	"	"
16.	$C_9H_{10}N_3CuCl$	Dark Green	" "	"	"	"	"	"	"	"
17.	$C_6H_4N_3CuCl$	Green	" "	"	"	"	"	"	"	"
18.	$C_6H_4N_3CuOH$	Yellowish Green	" "	"	"	"	"	"	"	"

TABLE 14

ELEMENTAL ANALYSIS FOR COPPER (11) COMPLEXES OF IMIDAZOLE, BENZIMIDAZOLE AND SUBSTITUTED BENZIMIDAZOLES

	COMPOUND	FORMULA	C		H		N		Cu		Cl	
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1.	Imidazole Copper (11) Chloride	$(C_3H_3N_2)CuCl$	20.8	20.4	1.4	1.8	14.6	14.0	40.6	40.8	23.9	24.2
2.	Benzimidazole Copper (11) Chloride	$(C_7H_5N_2)CuCl$	35.4	35.9	2.2	2.3	9.4	10.2	29.7	29.6	16.8	17.4
3.	2-Methylbenzimidazole Copper (11) Chloride	$(C_8H_5N_2)CuCl$	38.8	38.9	2.6	2.9	8.6	9.2	26.9	27.4	16.7	16.3
4.	2-Vinylbenzimidazole Copper (11) Chloride	$(C_9H_7N_2)CuCl$	41.6	41.8	2.9	2.8	8.2	8.8	26.0	26.0	15.3	15.4
5.	2-Ethylbenzimidazole Copper (11) Chloride	$(C_9H_9N_2)CuCl$	41.1	40.8	3.4	3.5	8.5	8.8	24.2	24.2	14.9	15.2
6.	2-Propylbenzimidazole Copper (11) Chloride	$(C_{10}H_{11}N_2)CuCl$	41.9	42.6	4.1	4.0	8.1	8.0	22.8	22.9	13.9	14.3
7.	2-Butylbenzimidazole Copper (11) Chloride	$(C_{11}H_{12}N_2)CuCl$	43.7	44.0	4.3	4.6	6.9	7.6	21.4	21.3	13.4	13.3
8.	2-Pentylbenzimidazole Copper (11) Chloride	$(C_{12}H_{13}N_2)CuCl$	45.9	45.8	4.5	4.9	6.8	7.1	16.3	16.8	12.6	12.7
9.	2-Decylbenzimidazole Copper (11) Chloride	$(C_{17}H_{25}N_2)CuCl$	50.0	50.7	6.0	6.2	5.4	5.8	12.8	12.9	10.1	10.2
10.	2-Stearylbenzimidazole Copper (11) Chloride	$(C_{24}H_{39}N_2)CuCl$	54.4	54.6	7.1	7.5	4.6	4.5	21.4	21.0	6.9	7.4
11.	2-Phenylbenzimidazole Copper (11) Chloride	$(C_{13}H_9N_2)CuCl$	48.1	47.8	3.3	3.1	7.0	7.1	21.3	21.6	12.2	12.4
12.	2-Benzylbenzimidazole Copper (11) Chloride	$(C_{14}H_9N_2)CuCl$	47.7	47.6	3.1	3.2	10.8	10.6	21.7	21.8	12.8	12.9
13.	2-Naphthylbenzimidazole Copper (11) Chloride	$(C_{17}H_{11}N_2)CuCl$	52.9	52.5	3.1	3.2	6.1	6.0	17.3	17.4	10.6	10.9
14.	2- -Hydroxyethylbenzimidazole Copper (11)Chloride	$(C_9H_9N_2O)CuCl$	40.8	40.6	3.0	3.4	10.6	10.6	24.2	24.2	13.7	13.8
15.	2- -Mercaptobenzimidazole Copper (11) Chloride	$(C_9H_9N_2S)CuCl$	39.5	39.2	2.9	3.3	8.8	10.2	23.8	23.2	12.6	12.8
16.	2- -Aminoethylbenzimidazole Copper (11) Chloride	$(C_9H_{10}N_3)CuCl$	36.9	37.6	3.1	3.3	13.9	14.7	22.9	22.4	12.1	12.4
17.	Benzotriazole Copper (11) Chloride	$(C_6H_4N_3)_{3/2}CuCl$	39.3	39.3	3.0	3.2	21.1	22.9	25.9	26.1	9.9	9.6
18.	Benzotriazole Copper (11) Hydroxide	$(C_6H_4N_3)_{3/2}CuOH$	41.6	41.4	3.2	3.5	23.7	24.1	26.9	27.4	-	-

3.3 COPPER (11) COMPLEXES OF QUADRIDENTATE BENZIMIDAZOLE DERIVATIVES.

The compounds bibenzimidazolyl copper (11), 1, 2 - bibenzimidazolylmethane copper (11), and 1, 2 - bibenzimidazolylethane copper (11) are discussed in this section. The purpose of investigating these compounds was to determine whether this series of ligands co-ordinated with copper (11) to give structures which allowed antiferromagnetic exchange to take place within the molecule similar to the bidentate complexes. Experimental data for the temperature variation of the susceptibility (table 19), elemental analysis (table 17), general physical properties (table 16) and room temperature magnetic moments (table 18) are shown at the end of this section.

The empirical formula, LCu, the configuration of the ligand molecule (figure 25) and the high thermal stability of the complexes suggest a polymeric structure. A polymeric structure is also indicated by the magnetic behaviour of the complexes. The room temperature magnetic moments are anomalously low and are in the range 1.30 ± 0.03 B.M. The temperature variation of the magnetic susceptibility is complex. However, theoretical curves obtained from equation (15) using the constants shown in table 15 and modified by the addition of 12.5 percentum of Curie Law behaviour, fit the experimental data. This indicates antiferromagnetic exchange interaction involving a large

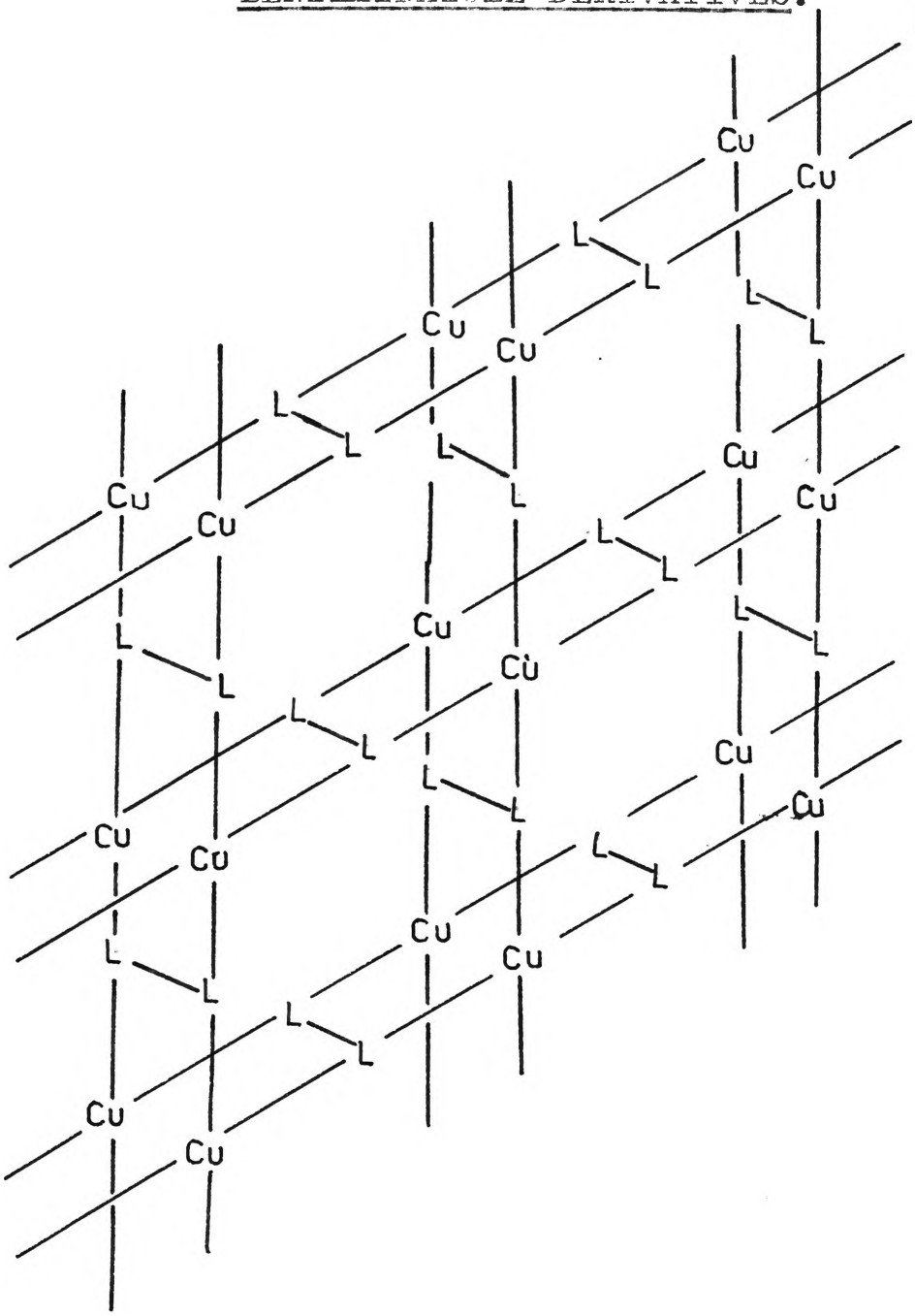
number of copper (11) atoms and consequently a polymeric structure for these complexes.

The suggested structure, shown in figure 22, represents an infinite two-dimensional double network of square planer copper atoms, each of them bonded to four nitrogen atoms. The observed antiferromagnetic exchange interaction may proceed along chains of copper atoms via bridging imidazole systems. The large copper-copper distances between neighbouring copper atoms preclude the possibility of direct copper-copper exchange. Interlayer exchange is unlikely because close approach of layers would be prevented by the bulky fused phenyl groups of the ligand molecules.

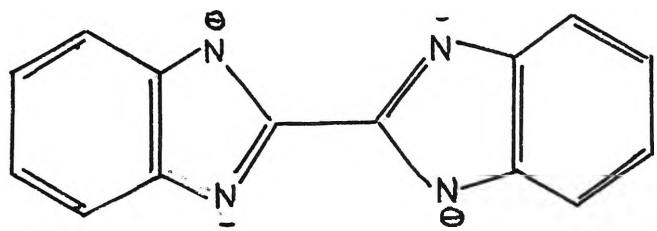
The magnetic behaviour of the quadridentate complexes is very similar to that observed for the bidentate complexes. This is indicated by the similar susceptibility versus temperature curves. A J value of 435 cm^{-1} and g value of 2.25 fits both series of complexes. The similarity of the magnetic behaviour probably reflects the use of a similar transmission medium, i.e. the imidazole groups, for the observed antiferromagnetic exchange interaction in both series of complexes.

FIGURE 22.

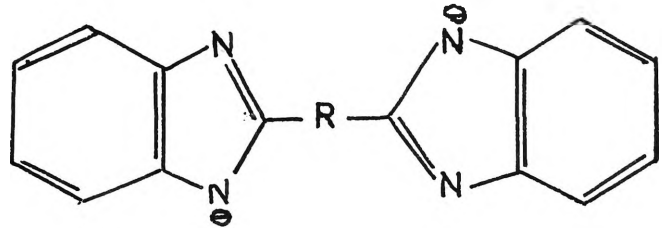
STRUCTURE OF COPPER(11) COMPLEXES OF QUADRIDENTATE BENZIMIDAZOLE DERIVATIVES.



where L - L is



or



and R is $-CH_2-$ or $-C_2H_4-$

TABLE 15

THEORETICAL Tc, g and J VALUES FOR COPPER (11) COMPLEXES OF QUADRIDENTATE BENZIMIDAZOLE DERIVATIVES.

C O M P O U N D	Tc ^{o}K	g	J(cm^{-})
Bibenzimidazolyl copper (11)	315	2.25	435
1,2-Bibenzimidazolylmethane copper (11)	315	2.25	435
1,2-Bibenzimidazolylethane copper (11)	315	2.25	435

TABLE 16

ELEMENTAL ANALYSIS OF COPPER (11) COMPLEXES OF QUADRIDENTATE BENZIMIDAZOLE DERIVATIVES

	COMPOUND	FORMULA	C		H		N		Cu	
			Found	Calc.	Found	Calc.	Found	Calc.	Found.	Calc.
1.	Bibenzimidazolyl Copper (11)	$(C_{14}H_8N_4)Cu$	57.3	56.5	3.4	3.4	18.5	18.8	21.5	21.3
2.	1,2-Bibenzimidazolylmethane copper (11)	$(C_{15}H_{10}N_4)Cu$	58.3	58.1	3.4	3.5	18.6	18.1	21.0	20.5
3.	1,2-Bibenzimidazolylethane copper (11)	$(C_{16}H_{12}N_4)Cu$	59.7	59.3	3.9	3.7	17.4	17.3	19.9	19.6

TABLE 17

GENERAL PHYSICAL PROPERTIES OF COPPER (11) COMPLEXES OF QUADRIDENTATE BENZIMIDAZOLE DERIVATIVES

	COMPOUND	COLOUR	BEHAVIOUR ON HEATING	SOLUBILITY						
				Water	Acetone	Isopropyl Alcohol	Chloroform	Ether	Ammonia	0.1N H.Cl
1.	$(C_{14}H_8N_4)Cu$	Pale Green	Decomposes leaving a black residue above 285°C.	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble on heating giving colourless solution.
2.	$(C_{15}H_{10}N_4)Cu$	"	" "	"	"	"	"	"	"	" "
3.	$(C_{16}H_{12}N_4)Cu$	"	" "	"	"	"	"	"	"	" "

TABLE 18

MAGNETIC DATA AT ROOM TEMPERATURE FOR COPPER (11) COMPLEXES OF QUADRIDENTATE BENZIMIDAZOLE DERIVATIVES

	COMPOUND	T°c	$10^6\chi_g$	$10^6\chi_m$	$-10^6\Delta$	$10^6\chi_m^1$	μ(B.M.)
1.	$(C_{14}H_8N_4)Cu$	21.7	3.03	534	201	735	1.32
2.	$(C_{15}H_{10}N_4)Cu$	21.6	2.93	527	213	740	1.33
3.	$(C_{16}H_{12}N_4)Cu$	21.9	2.76	496	224	720	1.28

TABLE 19

EXPERIMENTAL GRAM, MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS AT DIFFERENT TEMPERATURES FOR COPPER (11) COMPLEXES OF QUADRIDENTATE BENZIMIDAZOLE DERIVATIVES.

1. Bibenzimidazolyl Copper (11) -$(C_{14}H_8N_4)Cu$

T^oK	$10^6\chi_g$	$10^6\chi_m$	μ (B.M.)
97.8	3.69	893	0.84
105.3	3.44	831	0.84
119.2	3.31	801	0.88
142.8	3.26	789	0.95
166.9	3.22	780	1.02
195.4	3.03	732	1.07
251.4	3.03	732	1.22
294.7	3.03	735	1.32
316.9	3.03	732	1.37
374.2	2.90	701	1.45
397.6	2.82	682	1.48
440.3	2.58	624	1.49

TABLE 19 (Continued)

2. 1, 2-Bibenzimidazolylmethane Copper (11) - $(C_{15}H_{10}N_4)Cu$

$T^{\circ}K$	$10^6\chi_g$	$10^6\chi_m$	μ(B.M.)
98.5	3.45	870	0.83
103.9	3.29	819	0.83
115.7	3.17	799	0.86
139.4	3.13	790	0.94
168.6	3.11	785	1.03
189.9	3.06	771	1.09
240.7	2.99	753	1.21
294.6	2.93	740	1.33
310.2	2.90	731	1.35
354.1	2.84	715	1.43
368.1	2.78	700	1.44
401.7	2.71	683	1.49
428.8	2.51	634	1.48

TABLE 19 (Continued)

3. 1, 2-Bibenzimidazolylethane Copper (11) - $(C_{16}H_{12}N_4)Cu$

$T^{o}K$	$10^{6}\chi_{g}$	$10^{6}\chi_{m}$	μ (B.M.)
97.9	3.39	885	0.84
105.6	3.18	830	0.84
117.4	3.11	812	0.88
141.1	3.06	799	0.95
160.0	3.03	791	1.01
187.7	2.92	760	1.07
237.8	2.81	732	1.18
294.9	2.76	720	1.28
308.9	2.75	719	1.31
364.9	2.69	702	1.44
402.3	2.52	658	1.46
433.6	2.27	592	1.31

FIGURE 23.

MAGNETIC SUSCEPTIBILITIES AT DIFFERENT TEMPERATURES OF COPPER(11) COMPLEXES OF QUADRIDENTATE BENZIMIDAZOLE DERIVATIVES.

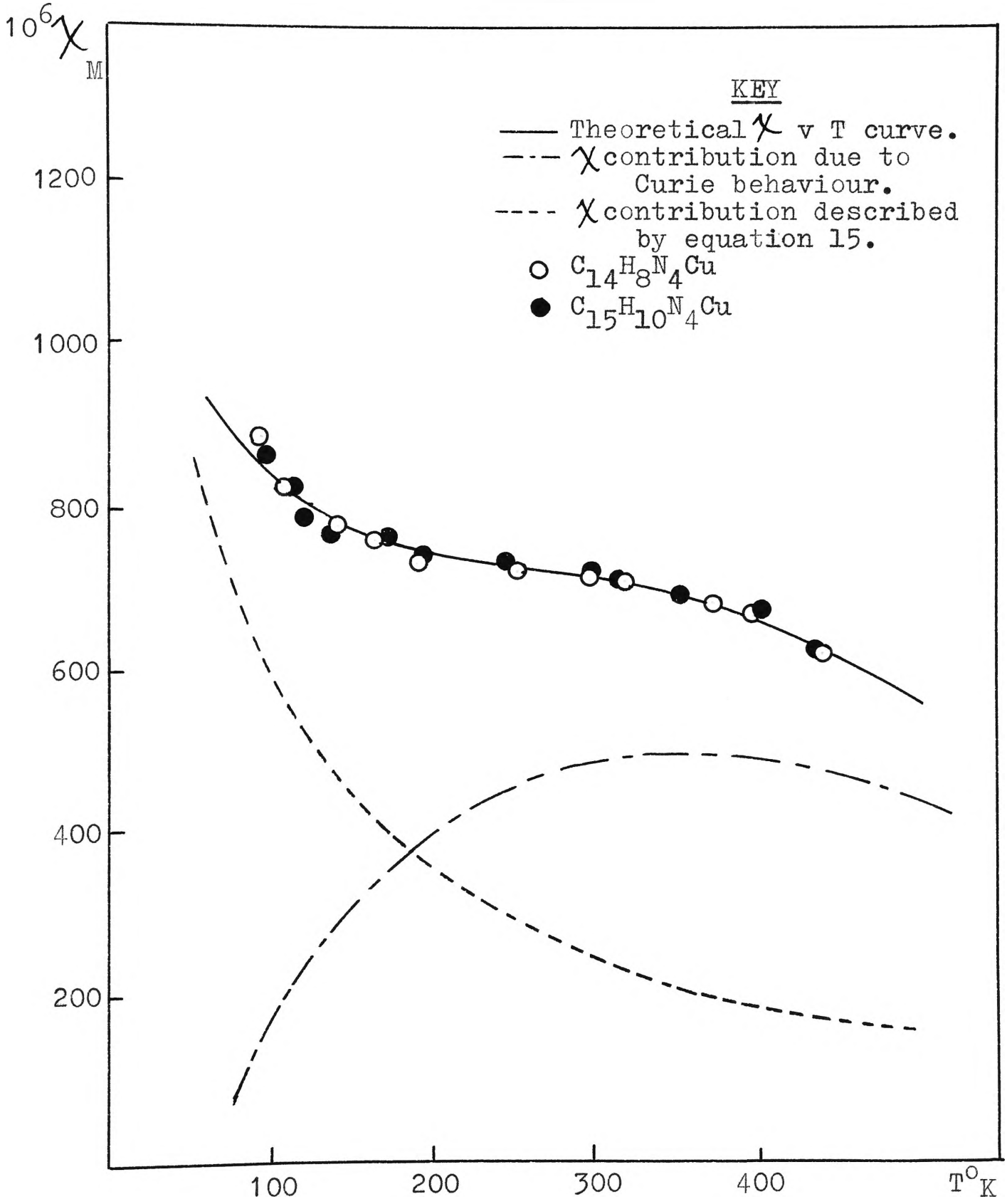


FIGURE 23 (cont.)

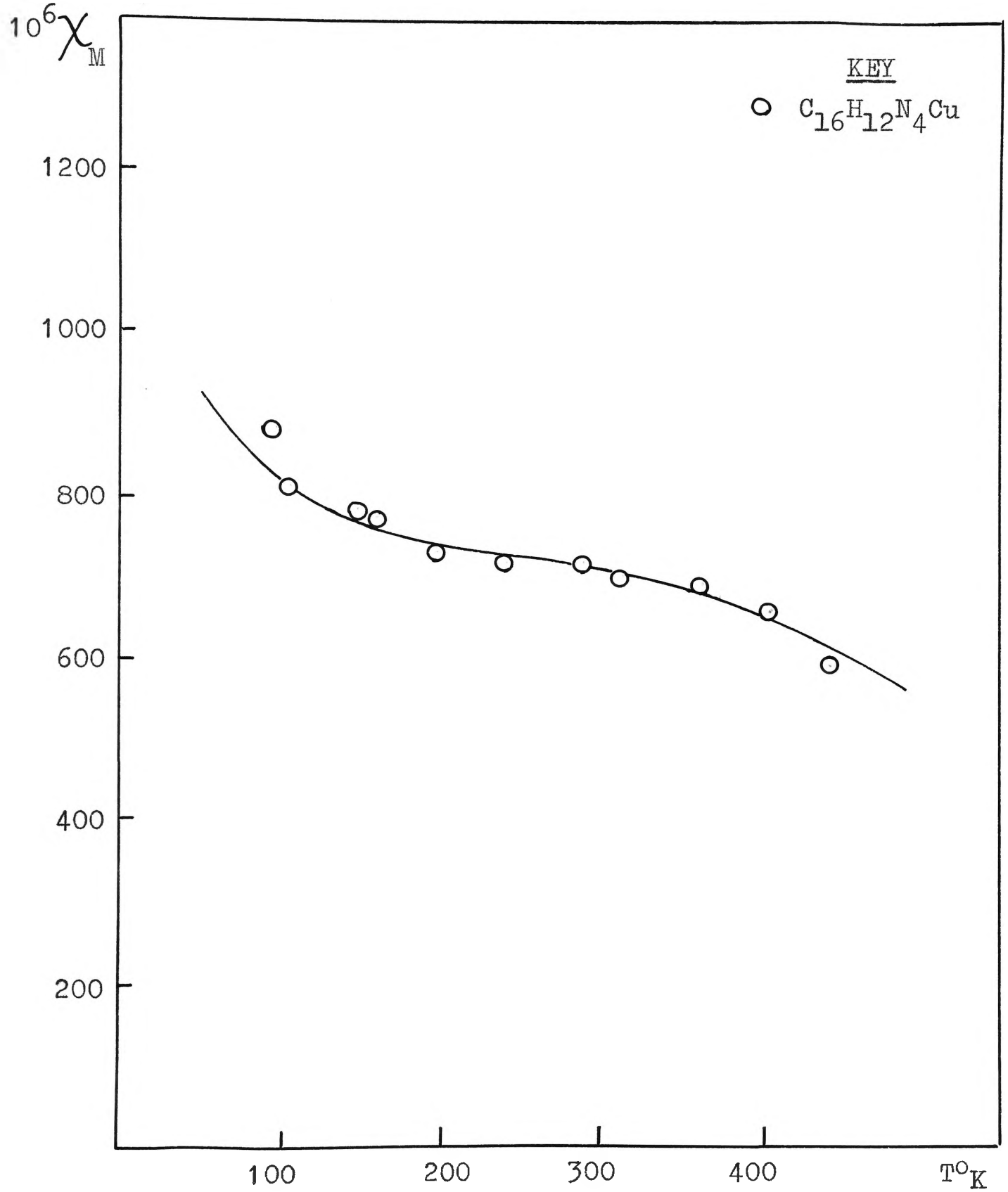


FIGURE 24.

MAGNETIC MOMENTS AT DIFFERENT TEMPERATURES OF COPPER(11) COMPLEXES OF QUADRIDENTATE BENZOTRIAZOLE DERIVATIVES.

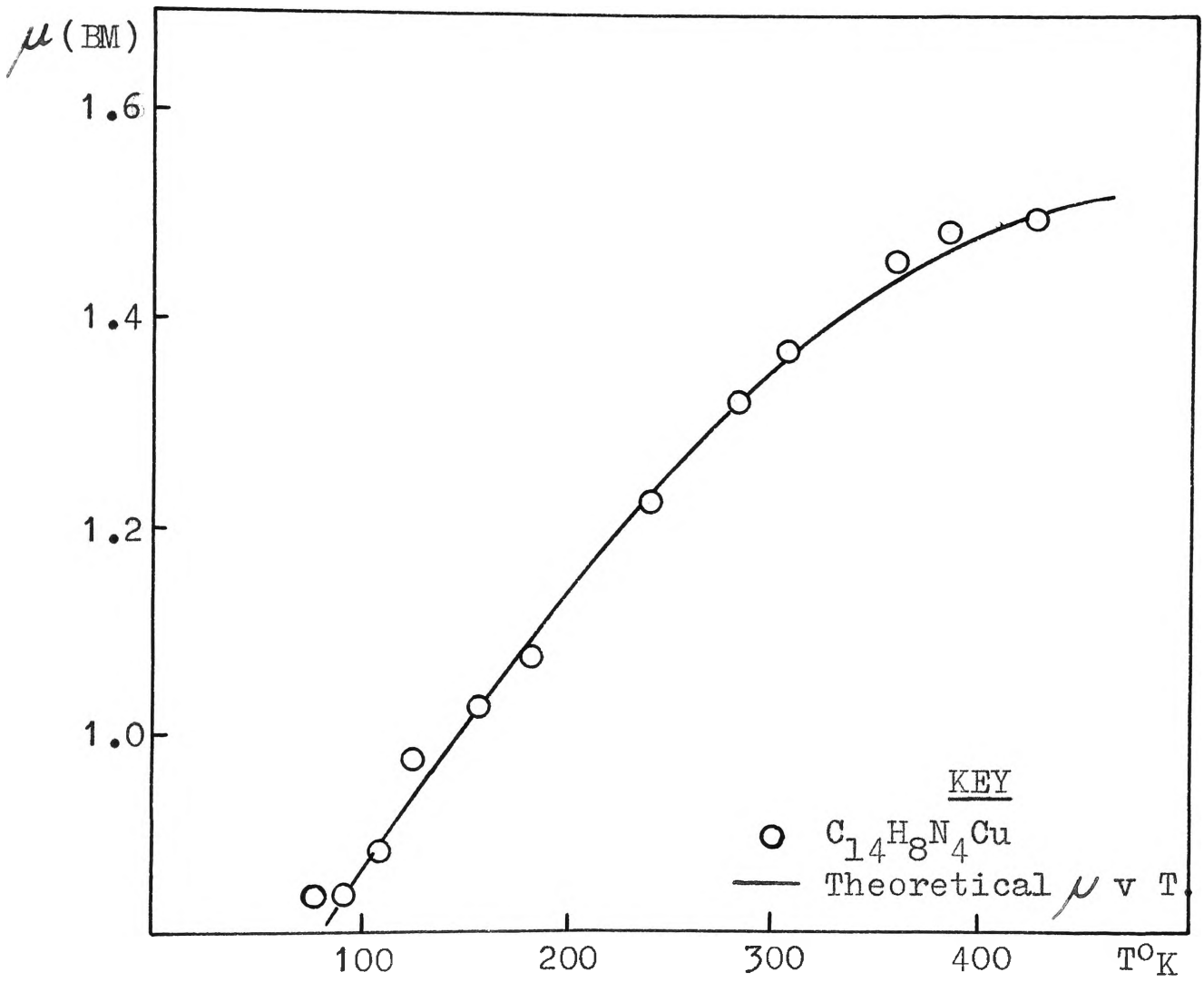
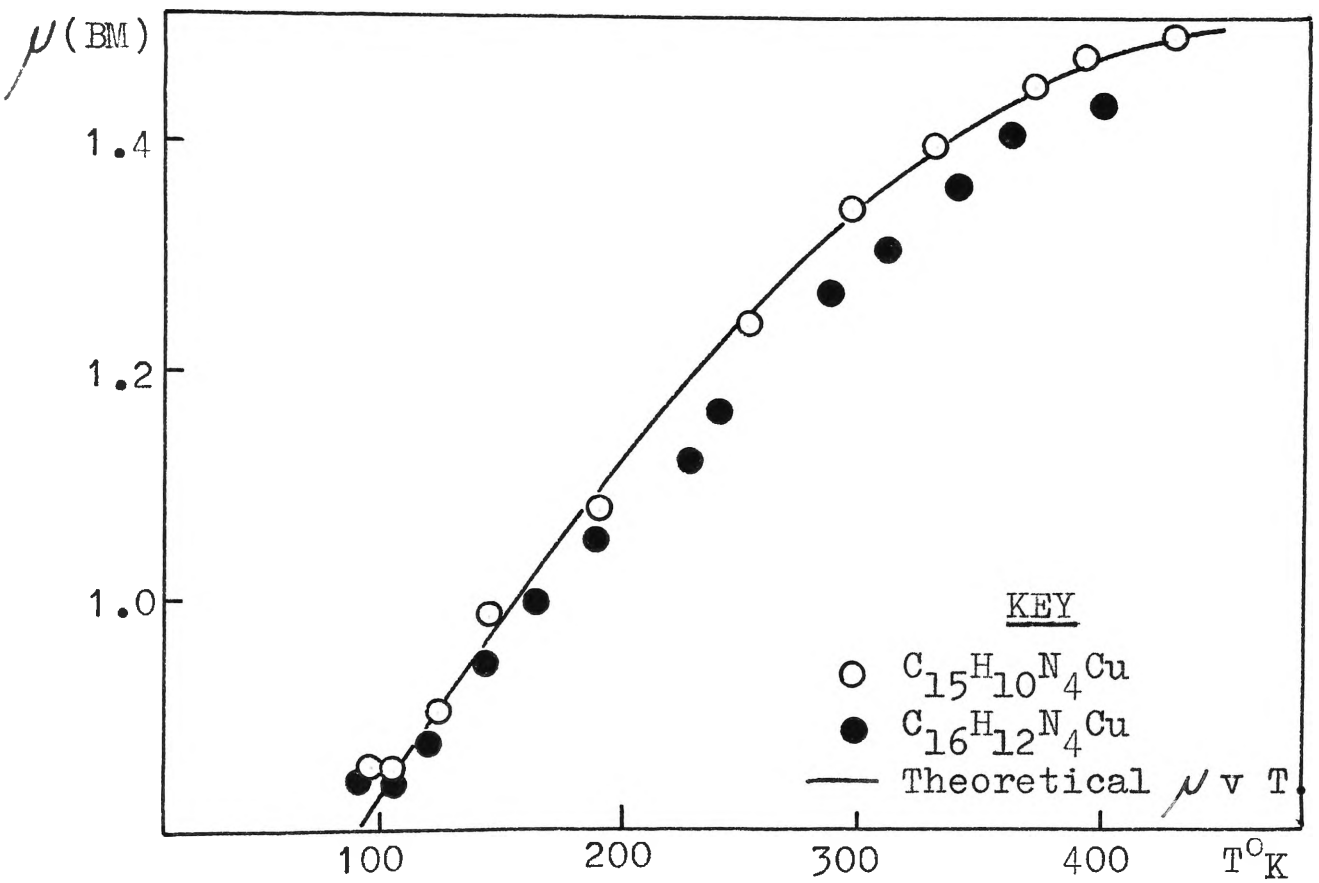


FIGURE 24 (cont.)



4.0 EXPERIMENTAL

4.1 PREPARATION OF LIGANDS

Table 20 summarises the analytical figures for the ligands. The letters in column 5 refer to the source of the material or method of preparation. In figure 24(a), the configurations of the ligands are illustrated.

A. A commercially available product manufactured by May and Baker, was recrystallised from ethanol.

B. Two substituted benzimidazoles were formed when O-phenylene diamine was heated with the appropriate carboxylic acid. The reaction involves an intermediate monoacyl derivative and subsequent ring closure. The appropriate acid and a molecular equivalent of O-phenylene diamine were heated under reflux. The mixture was dissolved in ethanol and any unreacted acid was neutralised to phenolphthalein with potassium hydroxide solution (5%).

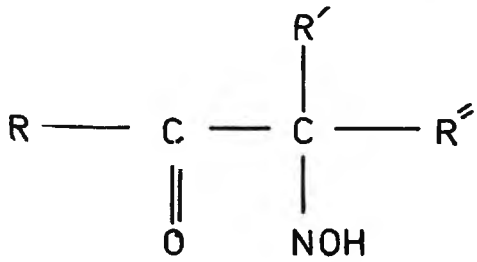
If the product did not separate immediately, it was extracted with ether and the compounds were recrystallised from aqueous ethanol (70%), subsequently from isopropyl alcohol, filtered, washed and dried over calcium hydroxide.

C. α-Benzoin Oxime.

A commercially available product was recrystallised from benzene.

FIGURE 24(a).

CONFIGURATION OF LIGAND MOLECULES.



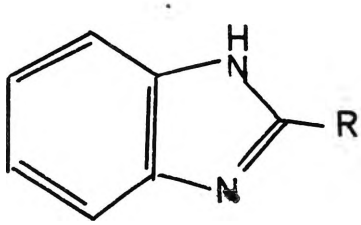
ACYLOIN OXIME

Where R and R" = $-C_6H_5$

and R' = $-H$, $-CH_3$ or $-C_6H_5$.

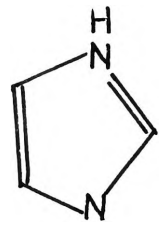
and where R and R" = $-C_4H_4O$

and R' = $-H$.

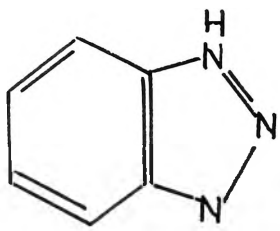


BENZIMIDAZOLE AND SUBSTITUTED BENZIMIDAZOLES.

Where R = $-H$; $-CH_3$; $-C_2H_3$; $-C_5H_{11}$; $-C_{10}H_{21}$; $-C_{17}H_{35}$; $-C_6H_5$; $-C_{10}H_7$; $-C_7H_7$; $-CH(NH_2)CH_3$; $-CH(OH)CH_3$; or $-CH(SH)CH_3$.

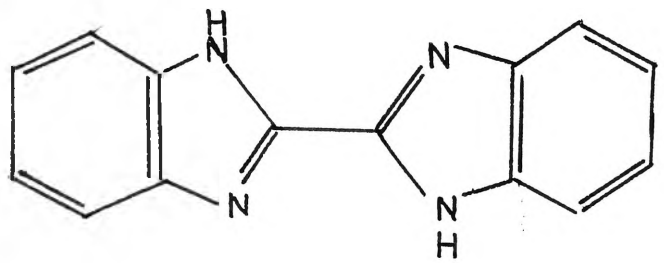


IMIDAZOLE.

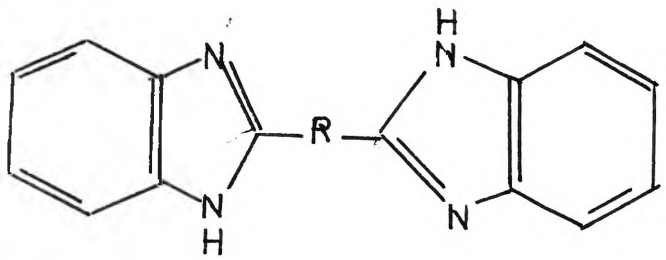


BENZOTRIAZOLE.

FIGURE 24a(cont.)



BIBENZIMIDAZOLYL.



SUBSTITUTED BIBENZIMIDAZOLE.

Where R = $-CH_2-$ or $-C_2H_4-$

D. α - Furoin Oxime.

Freshly distilled furfural was condensed with potassium cyanide according to Hartman and Dickes[87]. The furoin obtained was oximated with an excess of hydroxylamine hydrochloride in pyridine and methyl alcohol solution. The furoin oxime was finally crystallised from a mixture of absolute alcohol and petroleum ether.

E. α - Methylbenzoin Oxime.

Methylbenzoin was synthesized following the method described by Roger[88], methylmagnesium iodide was added to benzil. The oxime was prepared and purified in the same manner as 2,2' Furoin Oxime.

F. α - Phenylbenzoin Oxime.

Phenylbenzoin was prepared according to Acree[89]. The oxime was obtained and purified in the same manner as 2,2' - Furoin oxime.

TABLE 20

ANALYSIS OF LIGANDS

COMPOUND	C% Found	C% Req.	H% Found	H% Req.	N% Found	N% Req.	METHOD OF PREPARATION.	MELTING POINT °C Obs	MELTING POINT °C Recorded	O Found	O Calc.	S Found	S Calc.
1. Imidazole - $C_3H_4N_2$	52.8	52.9	5.8	5.9	41.2	41.2	A						
2. Benzimidazole - $C_7H_5N_2$	71.2	71.1	5.1	5.0	23.9	23.8	A	170-171	173[84]				
3. 2- Methylbenzimidazole-$C_8H_8N_2$	72.6	72.7	6.0	6.1	21.3	21.1	B	177-178	178[84]				
4. 2- Vinylbenzimidazole-$C_9H_8N_2$	75.0	75.0	5.7	5.6	19.5	19.4	B						
5. 2- Ethylbenzimidazole-$C_9H_{10}N_2$	73.9	74.0	6.8	6.9	19.3	19.2	B	180-181	177[84]				
6. 2- Propylbenzimidazole-$C_{10}H_{12}N_2$	75.0	75.0	7.5	7.6	17.5	17.5	B	159-160	157[84]				
7. 2- Butylbenzimidazole-$C_{11}H_{13}N_2$	76.6	76.7	7.1	7.0	16.4	16.2	B	156-158	157[84]				
8. 2- Pentylbenzimidazole-$C_{12}H_{14}N_2$	77.4	77.3	7.8	7.6	15.2	15.0	B	167-169	163[84]				
9. 2- Decylbenzimidazole-$C_{17}H_{26}N_2$	79.2	79.0	10.2	10.1	10.9	10.8	B						
10. 2- Stearylbenzimidazole-$C_{24}H_{40}N_2$	80.9	80.8	11.5	11.3	7.8	7.9	B	96- 98	94[84]				
11. 2- Phenylbenzimidazole-$C_{13}H_{10}N_2$	80.4	80.4	5.2	5.2	14.5	14.4	B						
12. 2- Benzylbenzimidazole	79.6	79.6	6.2	6.2	14.3	14.3	B	149-150					
13. 2- Naphthylbenzimidazole	83.5	83.6	5.0	4.9	11.5	11.6	B						
14. Indazole	71.2	71.1	5.3	5.1	24.0	23.7	A						
15. α-Benzoin Oxime	74.4	74.3	5.5	5.3	6.4	6.2	C	149-150	150-151[85]		14.2		
16. α-Furoin Oxime	58.5	58.3	4.0	3.9	6.9	6.7	D	151-158	160-161[86]		31.0		
17. α-Methylbenzoin Oxime	74.8	74.7	6.4	6.8	5.9	5.8	E	121-123			13.2		

TABLE 20 (Continued)

	COMPOUND	C% Found	C% Req.	H% Found	H% Req.	N% Found	N% Req.	METHOD OF PREPARATION.	MELTING POINT °C Obs	MELTING POINT °C Recorded	O Found	O Calc.	S Found	S Calc.
18.	α - Phenylbenzoin Oxime	79.6	79.2	5.8	5.7	4.2	4.6	F	148-151			10.5		
19.	Benzotriazole	60.4	60.5	4.5	4.3	35.6	35.3	A						
20.	1- Methylbenzotriazole	63.2	63.1	5.1	5.3	31.5	31.6	A						
21.	Benzothiazole	52.7	52.3	3.8	3.7	20.7	20.4	A						23.4
22.	2-α - Hydroxyethylbenzimidazole	66.8	66.7	6.1	6.2	17.4	17.3	B				9.9		
23.	2-α - Thioethylbenzimidazole	66.3	66.6	5.7	5.6	15.9	15.7	B						18.0
24.	2- α- Hydroxybenzylbenzimidazole	74.9	75.0	5.6	5.4	12.7	12.5	B				7.1		
25.	2- α- Aminoethylbenzimidazole	67.1	67.0	6.9	6.8	26.4	26.0	B						
26.	Bibenzimidazolyl	71.9	7.8	4.6	4.3	24.1	24.0	B						
27.	Bibenzimidazolylmethane	73.2	73.3	5.4	5.4	21.7	21.4	B						
28.	1,- - Bibenzimidazolylethane	72.2	72.7	4.8	4.9	22.8	22.5	B						
29.	1,2, - Bibenzimidazolylethane	73.9	73.8	6.7	6.7	21.7	21.5	B						

4.2 PREPARATION OF INDIVIDUAL COPPER (11) COMPLEXES

All complexes of bivalent copper investigated in this work were prepared by the following method. The appropriate ligand (2% by weight in 50% ethanol/water) was added dropwise to the appropriate cupric salt (2% by weight in water). The solution was gently warmed to promote coagulation. If precipitation did not occur, the solution was treated with 0.1N sodium hydroxide. The precipitate was collected and washed with four successive lots of water. The complexes were washed with isopropyl alcohol, dried at 80°C in a laboratory oven and subsequently stored in a vacuum desiccator.

4.3 ELEMENTAL ANALYSIS

Copper was determined iodometrically using sodium thiosulphate. Chloride was determined volumetrically by the method as devised by Mohr[97]. Carbon, hydrogen and nitrogen were determined by the usual methods.

4.4 DETERMINATION OF WEIGHT LOSS OF COMPLEX ON HEATING

A known amount of the compound was placed in a tared platinum crucible. The compound was heated to the predetermined temperature and maintained at that temperature until no change in weight occurred. The loss in weight was calculated as a percentage of the initial sample weight.

4.5 DETERMINATION AND CALCULATION OF MAGNETIC SUSCEPTIBILITIES

Magnetic susceptibilities were determined by the Gouy method (Figure 26). If an element of material (dV/dm) experiences a force (dF) along the field gradient (dH/dx) when placed in an inhomogeneous magnetic field of value H at a point dV, this force is given by the relationship:-

$$dF = H\ K\ dV\ \frac{dH}{dx} = H\ \ dm.\ \frac{dH}{dx} \quad \text{.....(i)}$$

where K is the volume susceptibility. The Gouy method is based upon the integration of this force from the region of maximum field (H, at the centre of the pole gap) to a region of approximately zero field (H_0). If equation (i) is integrated over this gradient it takes the form

$$F = 1/2\ A\ K\ (H^2 - H_0{}^2)$$

where A is the cross-sectional area of the specimen. When corrections are made for the diamagnetism of the tube and for the amount of air displaced by the specimen, equation (ii) becomes

$$F = 1/2\ A\ (H^2 - H_0{}^2)\ \ (K - K^1) + S$$

where K^1 is the volume susceptibility of the air.

Since for a specimen of constant cross-sectional area and length 1, the expression 1/2 A $(H^2 - H_0{}^2)$ is constant, introducing the density of the specimen it is possible to rewrite equation (13) in terms of the gram susceptibility as

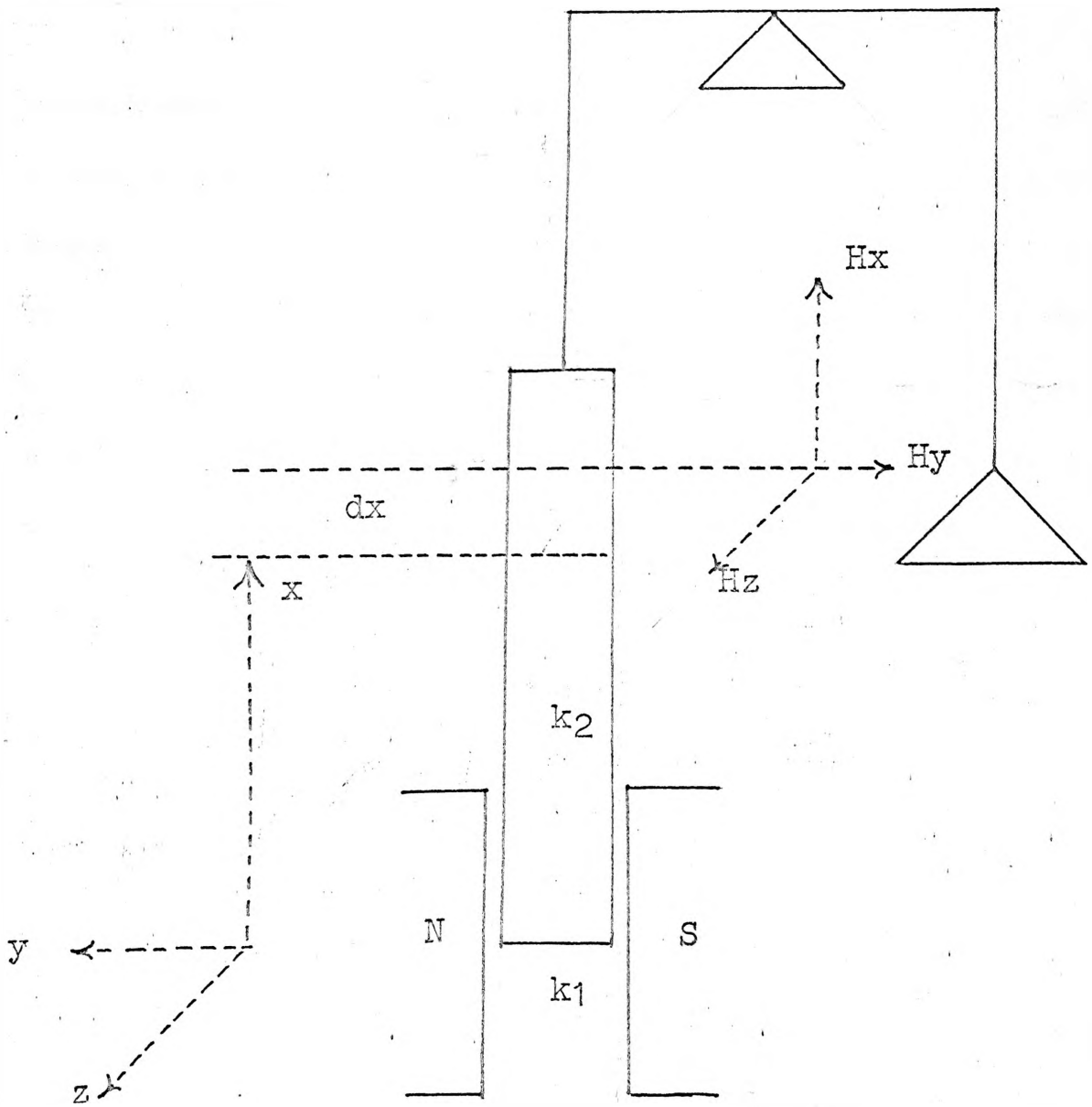
$$\chi_M = \frac{\alpha + \beta F^1}{W}$$

where F^1 (= F - S) is the force of the specimen (F being the observed force), α a constant to allow for the amount of air displaced, and W the weight of the specimen. The tube calibration constant β is determined by substitution into equation (i) for a compound of known susceptibility.

A number of magnetic standards are in common use. In this investigation both $Cu(SO_4)_2$, $5H_2O$ and Hg Co $(CNS)_4$ have been used as calibrants. Gouy tubes made of pyrex glass with an internal diameter of 4 mm. and a sample length of about 5 cm. were used in conjunction with a permanent magnet for the measurements carried out at room temperatures.

The apparatus used to determine the variation of magnetic susceptibilities with temperature was very similar to that discussed by Figgis and Nyholm. Gouy tubes (length = 10 cm, internal diameter = 3 mm.) made of pyrex glass were used which necessitated the determination of diamagnetic corrections for the tube over the temperatures at which studies were carried out. Temperatures were measured to an accuracy of $\pm$ 0.5 ^{o}K. Uniformity of packing was not readily achieved over the entire length of the tube with the result that measurements over a range of temperature were not as accurate as those determined at room temperature. The Gouy tubes were not calibrated against a standard compound; the susceptibility of any given compound at a particular temperature was determined by reference to its susceptibility at room temperature by means of the equation

Fig. 26. THE GOUY METHOD OF MEASURING MAGNETIC SUSCEPTIBILITIES



$$10^6 \chi^T = 10^6 \chi^{RT}{}_1 \cdot F_T{}^1 / F_{RT}{}^1$$

where $10^6 \chi^T$ is the susceptibility at the temperature being considered, $10^6 \chi^{RT}$ the susceptibility at room temperature and $F_T{}^1$ and $F_{RT}{}^1$ the force on the specimen at the temperature being considered and at room temperature respectively.

Measurements were made on each compound at two different field strengths to detect the presence of any field strength dependence in the magnetic susceptibility. This can be done by comparing the ratio of pulls obtained for a given compound with the ratio of pulls obtained at the same two field strengths with compounds whose magnetic susceptibilities are known to be independent of field strength.

5.0 REFERENCES

1. J. H. Van Vleck, Phys. Review, 1932, 41, 208; J. Chem. Phys. 1935, 3, 807.

2. B. N. Figgis and R. L. Martin, J. Chem. Soc., 1956, 3837.

3. Langevin.

4. B. N. Figgis and J. Lewis in "Modern Co-ordination Chemistry". (Editors: J. Lewis and R. G. Wilkins) Interscience, New York, 1960.

5. B. N. Figgis and J. Lewis, Progr. Inorg. Chem., 1964, 6, 37.

6. B. N. Figgis, Techniques of Inorganic Chemistry, 1965, 4, 139.

7. D. S. McClure, Some Aspects of Crystal Field Theory (Editors: T. Dunn, D. S. McClure and R. G. Pearson), Harper & Row, New York, 1965.

8. H. A. Kramers, Physica, 1934, 1, 182, See also P. W. Anderson, Phys. Rev., 1950, 79, 350.

9. B. Bleany and K. D. Bowers, Proc. Roy. Soc., 1952, A. 214, 451.

10. J. Lifschitz and E. Rosenbohm, Z. Electrochem, 1915, 21, 499.

11. B. C. Guha, Proc. Roy. Soc., 1951, A.206, 353.

12. G. Foex, T. Karantassis, N. Perakis, Compt. rendu, 1953, 237, 982

13. B. N. Figgis and R. L. Martin, J. Chem. Soc., 1956, 3837.

14. D. Polder, Physica, 1942, 9, 709.

15. Ross, I.G., Trans. Faraday Soc., 1959, 55, 1057.

16. Ross, I. G. and Yates J., Trans. Faraday Soc., 1959, 55, 1064.

17. Harris, C.M., Hoskins, B.F. and Martin, R.L., J. Chem. Soc., 1959, 3728.

18. Harris, C.M., Kokot, E., and Lenzer, S.L., Nature, 1962, 196, 471.

19. Harris, C.M., Kokot, E., Lenzer, S.L., and Lockyer, T.N., Chem. Ind. (London), 1962, 651.

20. Harris, C.M., and Martin, R.L., Proc. Chem. Soc., 1958, 259.

21. Inoue, M., Kishita, M., and Kubo, M., J. Chem. Soc. Japan, Pure Chem. Soc., 1963, 84, 758.

22. Inoue, M., Kishita, M., and Kubo, M., J. Chem. Soc. Japan, Pure Chem. Soc., 1963, 84, 759

23. Inoue, M., Kishita, M., and Kubo, M., presented at the Symposium on Structural Chemistry, Sendai, Japan, October 1963.

24. E. Kobot, Ph.D. Thesis, University of New South Wales, 1961.

25. Dubicki, L., Harris, C.M., Kokot, E., and Martin, R.L., Inorg. Chem., 1966, 5, 93.

26. Inoue, M., Kishita, M., and Kubo M., Acta Cryst., 1963, 16, 699.

27. Kishita, M., J. Chem. Soc. Japan, Pure Chem. Soc., 1962, 83, 264.

28. Forster, L.S., and Ballhausen, C.J., Acta Chem. Scand., 1962, 16, 1385.

29. Asai, O., Keshita, M., and Kubo, M., Naturwissenschaften, 1959, 12, 46.

30. Asai, O., Kishita, M., and Kubo, M., J. Phys. Chem., 1959, 63, 96.

31. Kondo, M., and Kubo, M., J. Phys. Chem., 1958, 62, 468

32. Kondo, M., and Kubo, M., J. Phys. Chem., 1958, 62, 1558.

33. Martin, R.L., and Waterman, H., J. Chem. Soc., 1959, 2960.

34. Nyholm, R.S., Proc. Chem. Soc., 1961, 273.

35. Kubo, M., Kishita, M., and Kuroda, Y., J. Polymer Sci., 1960, 48, 467.

36. Ploquin, J., Bull. Soc. Chem. France, 1951, 18, 757.

37. Ploquin, J., and Vergneau, C., Compt. rend., 1951, 232, 2439.

38. Van Nickert, J.N., and Schoening, F.R.L., Acta Cryst., 1953, 6, 227.

39. Van Nickert, J.N., and Schoening, F.R.L., Nature, 1953 36, 171.

40. Van Nickert, J.N., and Schoening, F.R.L., and de Wet, J.F., Acta Cryst., 1953, 6, 501.

41. M. Kishita, Y. Muot, and M. Kubo, Naturwissenschaften, 1957, 44, 372; ibid, 1957, 44, 612; Aust. J. Chem., 1957, 10, 386, ibid, 1958, 11, 309.

42. M. Kubo, Y. Kuroda, M. Kisnita and Y. Muto, Aust. J. Chem., 1963, 16, 7.

43. Y. Muto, Bull. Chem. Soc., Japan, 1960, 33, 1242.

44. G. A. Barclay, C. M. Harris, B. F. Hoskins and E. Kokot, Proc. Chem. Soc., 1961, 264.

45. J. V. Quagliano, J. Fuzita, G. Franz, D. J. Phillips, J. A. Walmaley and S. Y. Tyree, J. Am. Chem. Soc., 1961, 83, 3770.

46. R. L. Carlin, J. Am. Chem. Soc., 1961, 83, 3773.

47. S. Kida, J. V. Quagliano, J. A. Walmaley, and S. Y. Tyree, Spectrochim Acta, 1963, 19, 189.

48. Y. Kakinta, S. Kida and J. V. Quagliano, ibid., 1963, 19, 201.

49. Barclay, G.A., and Hoskins, B.F., J. Chem. Soc., 1965, 1979.

50. Kishita, M., Muto, Y., Inoue, M., and Kubo, M., 16th Annual Meeting of the Chemical Society of Japan, Tokyo, March-April, 1963.

51. Hatfield, W.E. and Paschal, J.S., Muro, Y., and Jonassen, H.B., Inorg. Chem., 1965, 4, 97.

52. Hatfield, W.E., and Paschal, J.S., J. Am. Chem. Soc., 1964, 86, 3888.

53. Vossos, P.H., Jennings, L.D., and Rundle, R.E., J. Chem. Phys., 1960, 32, 1590.

54. Willett, R.D., Dwiggins, C., Jr., Kruh, R.F., and Rundle, R.E., J. Chem. Phys., 1963, 38, 2429.

55. Cotton - Feytis, E., Ann. Chim. (Paris), 1925, 4, 9.

56. Machin, D.J., Martin, R.L., and Nyholm, R.S., J. Chem. Soc., 1963, 1490.

57. Martin, R.L., Nyholm, R.S., and Stephenson, N.C., Chem. Ind. (London), 1956, 83.

58. Edwards, A.J., and Peacock, R.D., J. Chem. Soc., 1959, 4126.

59. Barraclough, C.B., and Ng. C.F., Trans. Faraday Soc., 1964, 60, 836.

60. Newell and Montroll, Revs. Mod. Physics, 1953, 25, 353.

61. Wells, J. Chem. Soc., 1947, 1670.

62. Helmholz, J. Amer. Chem. Soc., 1947, 69, 886.

63. Hatfield, W.E., Piper, T.S., and Klabunde, U., Inorg. Chem., 1963, 2, 629.

64. Pfeiffer, P., and Glaser, H., J. Prakt. Chem. Soc., 1938, 151, 134.

65. Basolo, F., and Murmann, R.K., J. Am. Chem. Soc., 1952, 74, 5243.

66. Basolo, F., and Murmann, R.K., J. Am. Chem. Soc., 1954, 76, 211.

67. Mann, F.G., and Watson, H.R., J. Chem. Soc., 1958, 2772.

68. Mulay, L.N., and Selwood, P.W., J. Am. Chem. Soc., 1955, 77, 2693.

69. Kiriyama, R., Ibamoto, H., and Matsuo, K., Acta Cryst., 1954, 7, 482.

70. Martin, R.L., and Waterman, H., J. Chem. Soc., 1959, 1359.

71. Polder, D., Physica, 1942, 9, 709.

72. Graddon, D.P., J. Inorg. Nucl. Chem., 1961, 17, 222.

73. Bevan, J.A., Graddon, D.P., McConnell, J.F., Nature, 1963, 199, 373.

74. Hall, D., and Waters, T.N., J. Chem. Soc., 1960, 2644.

75. Calvin, M., and Barkelew, C.H., J. Am. Chem. Soc., 1946, 68, 2267.

76. Hewellyn, F.J., and Waters, T.W., J. Chem. Soc., 1960, 2639.

77. Kato, M., Jonassen, H., and Fanning, J., Chem. Reviews, 64, 122.

78. Koizumi, H., Osaki, K., and Watanabe, T., J. Phys. Soc. Japan, 1963, 18, 117.

79. Jarvis, J.A.J., Acta Cryst., 1962, 15, 964.

80. Haseda, T., Miedema, A.R., Kobayashi, H., and Kanda, E., J. Phys. Soc., Japan, 1962, 17, 518.

81. Kobayashi, H., and Haseda, T., Kanda, E., and Kanda, S., ibid, 1963, 18, 349.

82. Griffiths, R.B., Private Communication with Kobayashi, H. (See reference 81).

83. Halfield, W.E., McGuire, H.M., Paschal, J.S., Whyman, W.R., J. Chem. Soc., 1966, 9, 1194.

84. Wild, F., Characterisation of Organic Compounds, 2nd Edition, Cambridge University Press.

85. Beisteins Handbuch der Organischen Chemie, Fourth Edition, Berlin, 1935, Vol. V111, 175.

86. Ibid, Vol. X1X, 205.

87. Hartman, W.W., and Dickey, J.B., J. Am. Chem. Soc., 1933, 55, 1228.

88. Roger, R., J. Chem. Soc., 1924, 127, 523.

89. Acree, S.F., Ber., 1904, 37, 2758.

90. Gorter, J., Phys. Review, 1932, 42, 437.

91. Kokot, E., Personal Communication.

92. Feigl, F., Ber., 1923, 56, 2083.

93. Feigl, F., Sicher, G., and Singer, O., Ber., 1925, 58, 2294.

94. Suter, H. and West, P., Anal. Chim. Acta, 1955, 13, 501.

95. Anderson, P.W., Phys. Rev., 1959, 115, 2.

96. Goodenough, J.B., Phys. Rev., 1960, 120, 67.

97. Mohr, Analyst, 1880, 5, 123.

98. Reed, K.G. and Gallant P.E., Private Communication.

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